jct JOURNAL OF COATINGS TECHNOLOGY

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May 1984

Special Feature Issue: MILDEW & BACTERIA

CHICAGO '84
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OCTOBER 24, 25, 26

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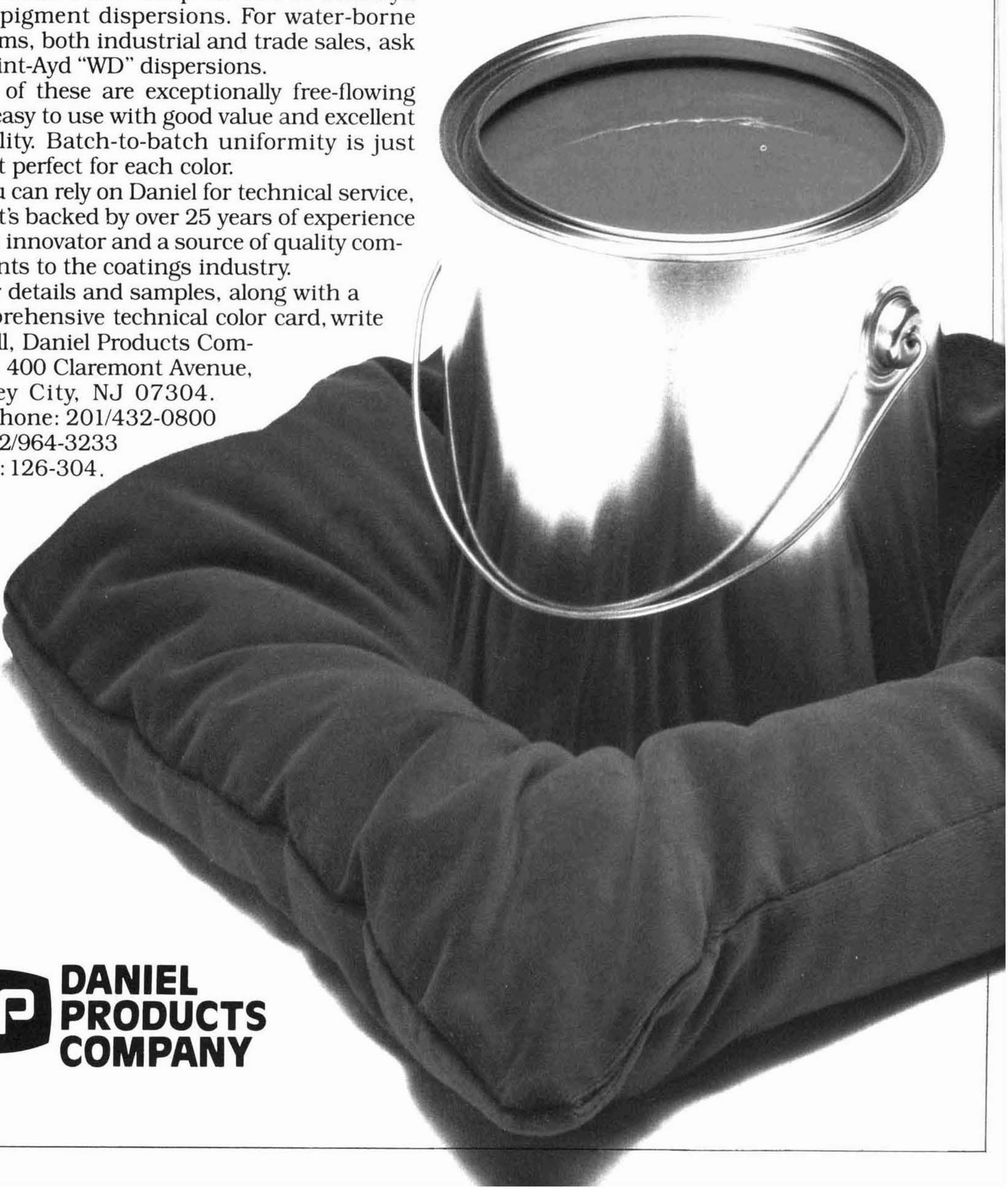

MAY 1984

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VOLUME 56 NUMBER 712

Special Feature Issue: Mildew and Bacteria

Technical Articles

33 Protection of Mildewcides and Fungicides from Ultraviolet Light Induced Photo-oxidation—P.D. Gabriele and R.M. Iannucci

51 Presence and Effects of Anaerobic Bacteria in Water-Based Paint I.—R.A. Oppermann and M. Goll

57 Mildewcide Testing and Ultrastructural Analysis with *Aureobasidium pullulans*—R.E. Crang and S.G. Robinson

65 Pigment Volume Concentration and an Interpretation of the Oil Absorption of Pigments—H.F. Huisman

81 Respirator Cartridge Evaluations for Paints Containing Isocyanates—J.F. Vasta

89 Determination of Pentachlorophenol Acrylate Purity by High Performance Liquid Chromatography—D.A. Frick

Federation News

18 **Booth Spaces Reserved for 1984 Paint Show; Exhibits Expanded to Five Halls in Chicago**

Departments

Comment 8 **Leo Roon—The Man and His Role in Our Industry**

Abstracts 13

Government and Industry 22 **Coast Guard Buoys Subject of Two-Year Battelle Study**

Committee Activities 30 Cooperative Mildew Research Undertaken by Eight Societies

Society Meetings 91

Federation Membership Anniversaries 92

Future Society Meetings 93

Elections 94

Meetings/Education 95 **Southern Society Draws Attendance of 447 to 50th Anniversary Meeting in Florida**

People 97

Obituary 98 **Walter F. Kuster, Federation Past-President, Dies**

Literature 99

Letters to the Editor 100 **Reader Comments on Efficiency of Ball Mills**

Book Review 101 **Organic Coatings: Science and Technology, Vol. 5**

Coming Events 102

Humbug from Hillman 104 **Dixie Dictionary; Campaign Reports; and More**

BPA

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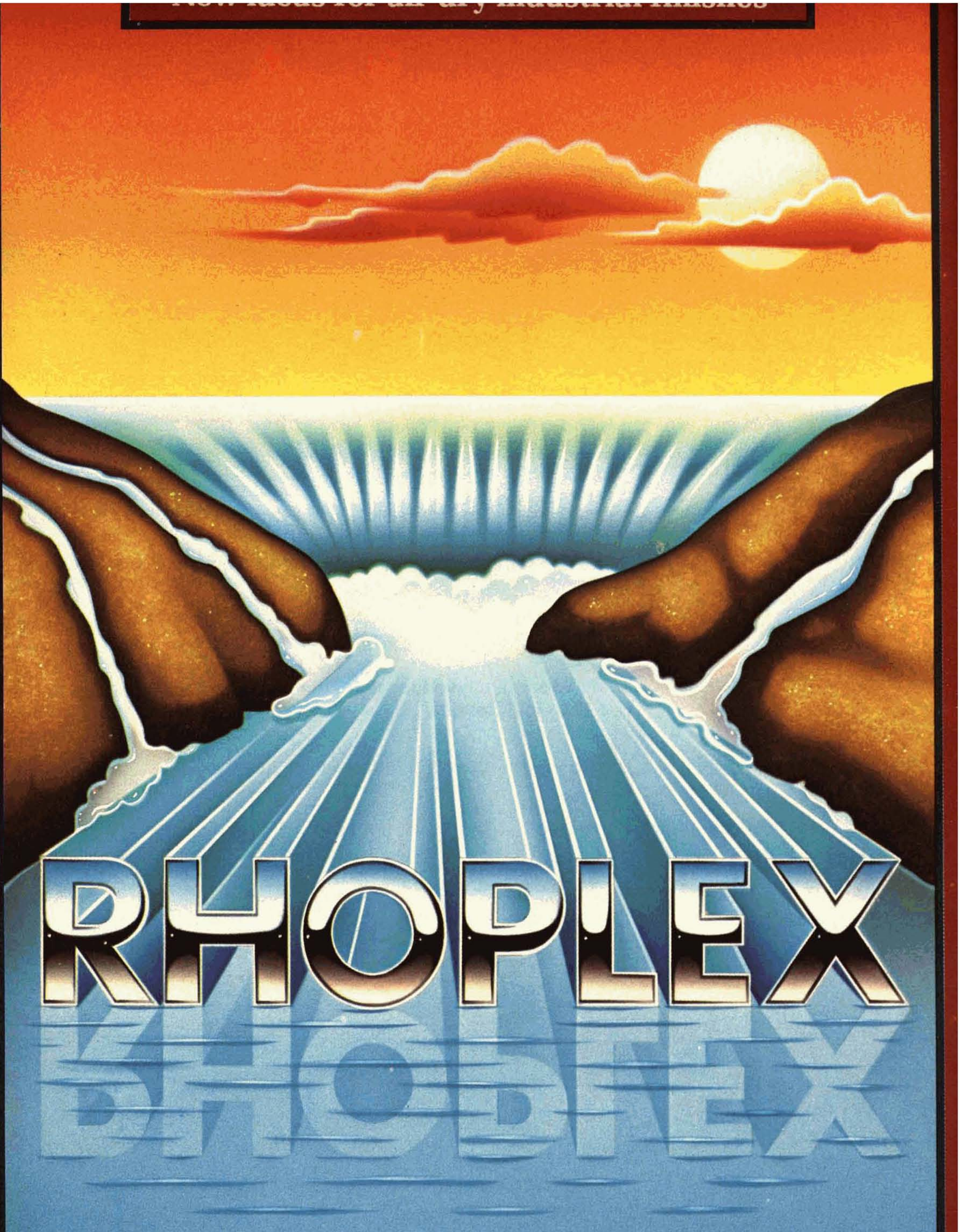
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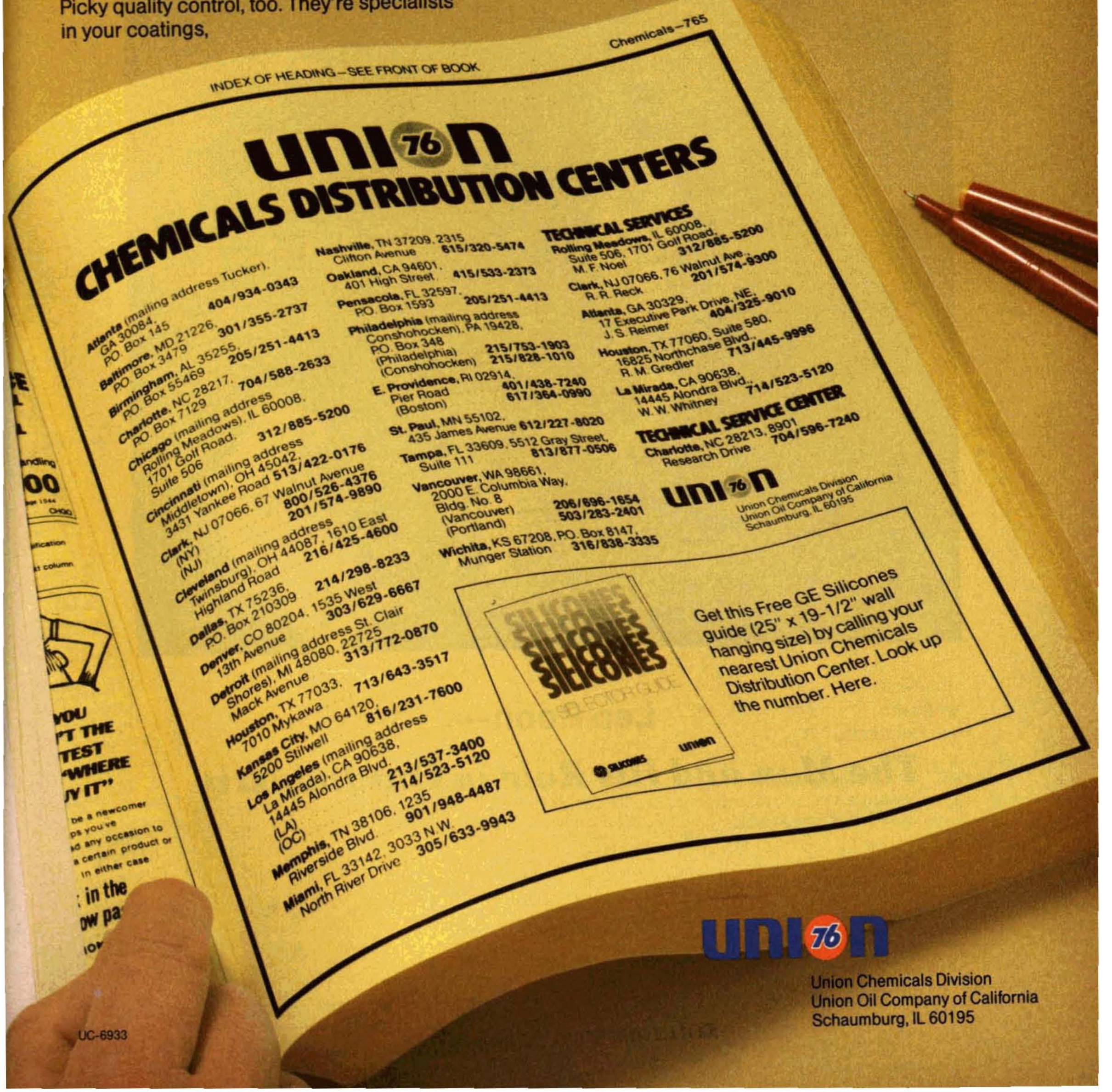

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INDEX OF HEADING—SEE FRONT OF BOOK

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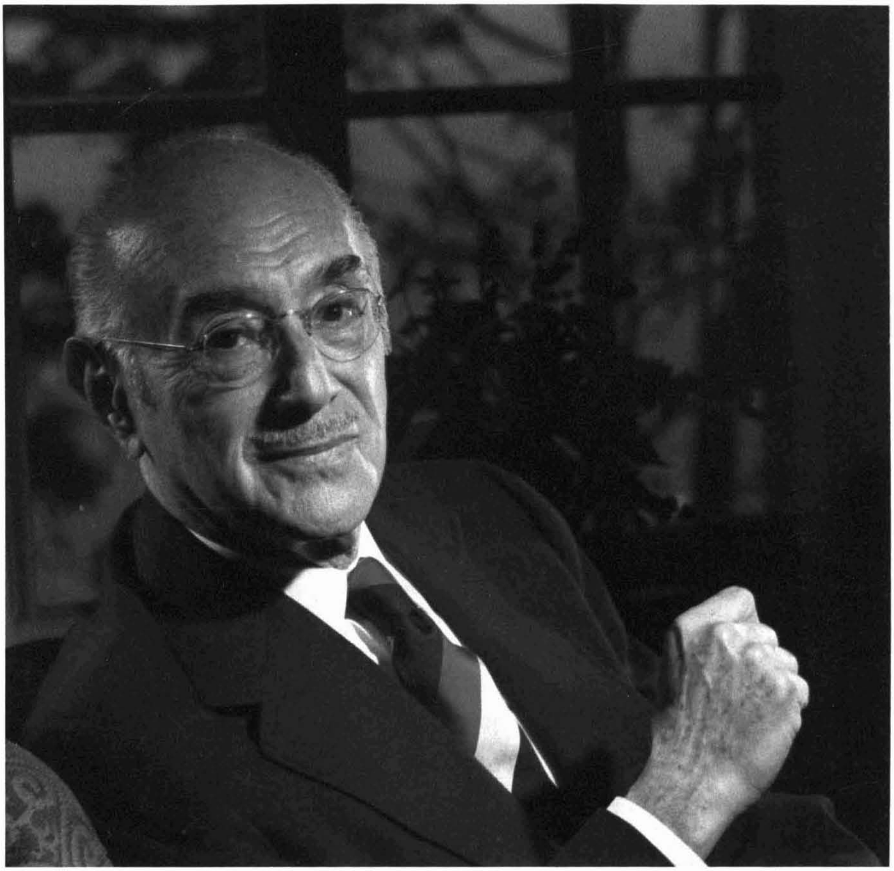

Leo Roon—

The Man and His Role in Our Industry

With Leo Roon's death on December 7, 1983, the industry lost one of its pioneers and most colorful personalities.

Leo was a self-made man, the prototype of the successful entrepreneur whose vision and drive significantly contributed to the transformation of the coatings industry from a craft to a technology and science.

When Leo founded Roxalin Flexible Finishes Company in 1924 he assembled a group of very bright young chemists and instilled in them his own sense of purpose and perfection. The result: Roxalin developed "top-of-the-line" and innovative coatings which commanded premium prices. So superior were many of their products that in 1947 big Interchemical Corp. (later Inmont) decided to buy out this hard-to-beat competitor.

A further compliment to Leo's team was the eagerness with which other coatings companies vied for former Roxalin chemists. For many years Roxalin alumni were widely encountered in top technical positions all over the country.

In his continued quest for ever better coatings, Leo recognized that standardization of *all* components was the key to reliable performance. Metallic driers were notoriously unreliable components. Their performance depended on the mood and the varying skills of the old-time varnish cookers. When Leo found out that metallic driers could also be made by controlled chemical reactions he saw that here was a product line the industry had been waiting for. Soon afterwards the Nuodex "Three Little Bottles" of lead, manganese, and cobalt driers were found on the shelf of every coatings and ink laboratory. They were only the first of a growing line of special purpose additives developed by Nuodex since 1932.

In 1954 Leo sold the company to Heyden Chemical which finally became part of Tenneco. Recently, Nuodex has been resurrected as an independent company.

Since then Leo devoted his inexhaustible energies to a host of other enterprises and activities, among them art. He himself became an accomplished sculptor whose works were exhibited.

What made Leo so successful in everything he touched was not just his vision, his technical and business acumen, his capacity for detail, and his superb gift for promoting *products.* He was equally adept in selecting and leading *people.* He commanded their loyalty, respect, and affection by a combination of personal charm, by his genuine interest in his associates, by his boundless intellectual curiosity, by his infectious enthusiasm, and last but not least by his generosity. The educational, medical, artistic, social, and charitable causes to which he gave not only money but his time and personal effort are legion. (See the Obituary in the February 1984 issue of the JOURNAL OF COATINGS TECHNOLOGY). High among the beneficiaries was the FSCT. The annual Roon Awards for outstanding technical papers stand as an enduring monument to his generosity, but even without it he will be remembered for the contributions he made to the advances of our industry. Those of us who knew him personally will remember him first and foremost as a friend and an extraordinary human being.

Fred Daniel

—FRED DANIEL,
Consultant
Princeton, NJ

(Mr. Daniel was a long time associate and friend of Mr. Roon. They began their relationship some 33 years ago at Nuodex, and, when Mr. Daniel started Daniel Products Co., Mr. Roon became its first outside stockholder. These shares were later donated to the Roon Foundation which funds the annual Roon Awards—Ed.)

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Abstracts of Papers in This Issue

PROTECTION OF MILDEWCIDES AND FUNGICIDES FROM ULTRAVIOLET LIGHT INDUCED PHOTO-OXIDATION—P.D. Gabriele and R.M. Iannucci

Journal of Coatings Technology, 56, No. 712, 33 (May 1984)

The biological activity of organic and organometallic biocides (fungicides including, mildewcides, antifoulants, pesticides, etc.) can be significantly diminished by photo-oxidation from terrestrial solar radiation. Photo-oxidation reduces biocide efficacy to an extent that a coating service life is lost as a result of biological surface defacement.

The purpose of this study was to determine whether organic and organometallic mildewcides and fungicides can be protected from the effects of ultraviolet photo-oxidation. The methodology demonstrates the protection of mildewcides and fungicides through the use of hydroxyphenyl benzotriazole ultraviolet light absorbers and/or hindered tetraalkyl piperdinol compounds. The evidence developed demonstrates a practical application of a theoretical analysis of mildewcide photo-oxidation. Laboratory analysis and determination of the effectiveness of mildewcide stabilization was accomplished by thin layer chromatography (TLC) and electron capture gas chromatography (ECGC). A simple accelerated laboratory procedure is described for testing and analysis of biocide breakdown and stabilization.

The concept of mildewcide stabilization was additionally supported through a statistical analysis of variance of exterior exposed samples representing all the levels of stabilized formulations compared to all the levels of unstabilized formulations.

Results show that the biological activity of stabilized fungicides and mildewcides in those coatings exposed to terrestrial ultraviolet radiation is maintained when stabilized with hydroxyphenyl benzotriazole and/or a tetraalkylpiperdinol light stabilizing compound.

PRESENCE AND EFFECTS OF ANAEROBIC BACTERIA IN WATER-BASED PAINTS. I—R.A. Oppermann and M. Goll

Journal of Coatings Technology, 56, No. 712, 51 (May 1984)

Water-based paints are subject to microbial invasion resulting in spoilage. Analysis of such spoiled paints frequently results in no known chemical or biological cause being found. Bacteria growing in the absence of oxygen (anaerobically) could cause some of the deterioration, but would not be found in the aerobic culture methods normally used. Accordingly, many paint and paint raw material samples, some of which were spoiled, were cultured under anaerobic conditions. Anaerobic bacteria which reduce viscosity and cause malodors and discoloration were found. The quantity, identification, degradation activity, biocide sensitivity, and prevention of the bacteria found are discussed.

MILDEWCIDE TESTING AND ULTRASTRUCTURAL ANALYSIS WITH *AUREOBASIDIUM PULLULANS*—R.E. Crang and S.G. Robinson

Journal of Coatings Technology, 56, No. 712, 57 (May 1984)

Five commercial non-metal-containing mildewcides were assessed for their inhibitory levels in defined liquid cultures of *Aureobasidium pullulans*. The results of culturing, light microscopy, and scanning and transmission electron microscopy showed one mildewcide to be the most effective at sublethal concentrations in the inhibition of growth and pigment production. At low concentrations, four of the agents promoted melanization to varying degrees, although growth was still decreased. At sub-inhibitory levels each agent induced some amount of ultrastructural damage as seen using transmission electron microscopy. Although all were effective at high concentrations in inhibiting growth of *A. pullulans*, certain agents allowed for the growth of bacteria in laboratory stocks.

Papers to Be Featured in the June Issue

Influence of Co-Solvents on the Film Properties of Water-Soluble Alkyds—Toronto Society for Coatings Technology

UV Curing of Acrylate Coatings by Laser Beams—C. Decker

Kinetics and Mechanism of Film Growth for the Cathodic Electrodeposition Process from Epoxy Resin-Curing Agent Latexes—M.S. El-Aasser, J.W. Vanderhoff, C.C. Ho, A. Humayun, and M.F. Abdel-Bary

Internal Stress of the Epoxide Resin Coatings Having Different Network Structures—M. Shimbo, M. Ochi, and K. Arai

The Simplex Mixture Screening Design in Coatings Research—K.K. Hesler, J.R. Lofstrom, J.A. Greenwald

Abstracts of Papers in This Issue (Continued)

PIGMENT VOLUME CONCENTRATION AND AN INTERPRETATION OF THE OIL ABSORPTION OF PIGMENTS—H.F. Huisman

Journal of Coatings Technology, 56, No. 712, 65 (May 1984)

A new description for the pigment volume concentration, PVC, is given. It is based on the average effective density of the aggregated particles as these particles are present, e.g. in dispersions, in coating layers, and in oil absorption pastes.

The average effective particle density can be measured by mercury porosimetry.

In this paper, the model is applied to pigment powder packings, e.g., bulk and tap densities, and to oil absorption pastes. For powder packings good agreement is obtained with model calculations. For oil absorptions, the mathematical description of the OA paste contains three contributions; these are: (1) the average effective particle density; (2) the packing of the particles; and (3) the wettability of the particles by the oil.

The contribution of the adsorbed oil layer is only of minor importance. It is shown that the generally accepted description for the oil absorption, e.g. as formulated by Stieg, is an extreme case of the model given in this paper.

This model clarifies why in the past it was not possible to solve the problem of how to adjust exactly the OA-measurements or the powder compaction to give pigments packings that correlate with CPVC's derived from actual paint results.

RESPIRATOR CARTRIDGE EVALUATIONS FOR PAINTS CONTAINING ISOCYANATES—J.F. Vasta

Journal of Coatings Technology, 56, No. 712, 81 (May 1984)

Organic vapor respirator cartridges have been evaluated for use with Imron® and Centari®, under conditions which approximate field conditions. These enamels will henceforth be referred to as Enamel A and Enamel B, respectively. Enamel A is a urethane coating, Type V, according to the ASTM designation, which contains traces of hexamethylene diisocyanate and a mixture of solvents, primarily ethyl acetate and Cellosolve® acetate. Enamel B is a modified acrylic coating, which contains traces of hexamethylene diisocyanate and a mixture of xylenes, toluene, and a variety of other solvents. Although solvent breakthrough was observed under some conditions, isocyanate breakthrough was not observed in any test. During four-hour exposures to Enamel A, neither solvent nor isocyanate breakthrough was observed with the Willson Products R21 organic vapor cartridge. On exposure of this cartridge to Enamel B, acetone breakthrough, followed by other solvents, was observed after 10 hours, but, even after 25 hours, isocyanate breakthrough was not observed. The prefilters used in these studies, R15 and R16, were interchangeable. Ethyl acetate broke through the Mine Safety Appliances organic vapor cartridge (part number 459315) and prefilter (part number 448842) after 15 hours, but isocyanate had not broken through even after 18 hours of exposure to Enamel A. Since ethyl acetate has an odor threshold of 50% recognition at approximately 13 ppm, it can serve as an indicator of the effective end of the cartridge life.

DETERMINATION OF PENTACHLOROPHENOL ACRYLATE PURITY BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY—D.A. Frick

Journal of Coatings Technology, 56, No. 712, 89 (May 1984)

A method for the separation and quantification of pentachlorophenol acrylate, a fungicidal monomer, has been developed. The method uses non-aqueous reversed phase high performance liquid chromatography (HPLC). The chromatography was accomplished using a mobile phase of 9/1 methanol/tetrahydrofuran (V/V), a C18 column, and ultraviolet detection at 254 nm. The separation was complete in less than five minutes.

An estimate of the amount of free pentachlorophenol was also obtained using this method.

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ISOPAR solvents offer you lower surface tension than you can expect from typical hydrocarbon solvents. That provides better wetting of substrates by coatings, inks, adhesives and other types of resins. It also means you'll get improved dispersibility of pigments and reduced foaming during the processing and application of water-based products (without side effects).

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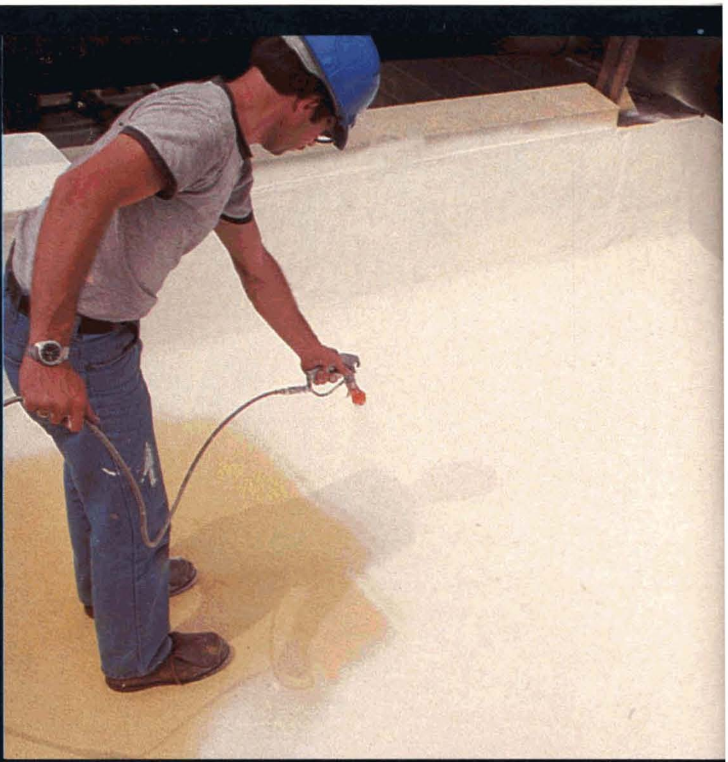
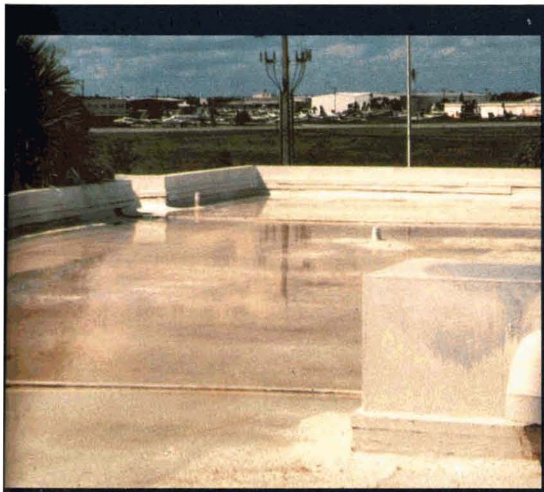
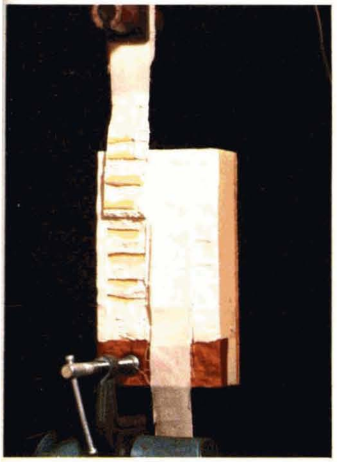


The reflective roof mastic based on RHOPLEX EC technology was spray applied on a roof in a heavy industrial environment in Pennsylvania. The photo at the lower right shows the same roof more than one year later.

INDUSTRY A BIG ACRYLIC FAVOR



This roof in Florida demonstrates how a roof mastic based on RHOPLEX EC-1895 acrylic retains its initial integrity under ponded water conditions.



The foam actually tore during peel adhesion testing on an Instron unit documenting adhesion of the mastic based on RHOPLEX EC-1791 acrylic.

Offer Roof Mastics Based on New RHOPLEX™ EC Technology

Introducing RHOPLEX® EC-1895 emulsion for superior resistance to water ponding conditions and RHOPLEX EC-1791 emulsion for superior adhesion to polyurethane foam. Acrylics from RHOPLEX EC technology are well known for:

- **Long term durability**
- **Long lasting flexibility even at low temperatures**
- **Superior dirt pick-up resistance and reflectivity**

RHOPLEX EC-1685 acrylic is the standard, when water ponding and adhesion are not problems.

For flat roofs with potential water ponding problems, the new RHOPLEX EC-1895 acrylic helps to keep bulk water from passing through the protective coating. Acrylics are known as breathers, not water vapor barriers. They transmit low levels of water vapor through the coating and thereby resist the formation of vapor traps in the building.

Another new roof mastic polymer, RHOPLEX EC-1791 provides elastomeric coatings with superior wet and dry adhesion to low and high density polyurethane foam.

Do your roofing contractors the favor of providing a seamless coating based on RHOPLEX EC technology. It goes on faster than sheets, eliminates hot tars, and reduces customer call backs. This saves time and money.

All you need to do to profit from this business opportunity is to combine your paint formulating know-how with RHOPLEX EC technology. Find out more about the product-line of acrylic polymers designed specifically for roof mastics. Write to Rohm and Haas Company, Marketing Services Department, Independence Mall West, Philadelphia, PA 19105.

ROHM AND HAAS
PHILADELPHIA, PA. 19105

Federation News

All Booth Spaces Reserved for 1984 Paint Show; Exhibits Expanded to Five Halls in Chicago

The 49th Paint Industries' Show, being held at the Conrad Hilton Hotel in Chicago, October 24–26, has expanded to include the North Hall in the hotel. This will be used in addition to the East and West Halls, and the Continental Room and International Ballroom, making the 1984 Paint Show the largest in Federation history in terms of exhibit space (45,000 plus sq. ft.) and exhibitors (almost 200).

The Show, being held in conjunction with the 62nd Annual Meeting of the Federation, is the only national exhibit of raw materials and equipment used in the manufacture of paints and related coatings, and participating firms will have their top technical personnel on hand to discuss the latest developments in coatings manufacturing technology.

Exhibit hours will be 12:00 to 5:30 pm on Wednesday, October 24; 9:30 am to 5:30 pm on Thursday, October 25; and 9:30 am to 3:00 pm on Friday, October 26.


CHICAGO—View looking south from the North Avenue Beach to the John Hancock Center and Lake Point Tower

Annual Meeting Program

The 62nd Annual Meeting of the Federation will open on Wednesday morning, October 24, in the Conrad Hilton, and Program Chairperson Darlene Brezinski, of DeSoto, Inc., has announced the theme, "Appearance and Protection—Essential to Our Lifestyle." She and her Program Steering Committee are developing a schedule of presentations around this topic.

Headquarters Hotel

The Conrad Hilton will serve as headquarters hotel. Other hotels with blocks of rooms set aside for the Annual Meeting are the Americana Congress, Continental, Essex Inn, Hyatt Regency, McCormick Center, and Palmer House.

Room Reservations

All requests for rooms and suites must be sent to the Federation office on the official housing form which has been mailed to all members and is included in this issue (see pages 23-27). Additional housing forms are available from the Federation headquarters office.

Registration Fees

Advance registration is available for $50 for members and $65 for non-members. Fee for spouses activities is $35 in advance.

Once again there will be a special registration fee of $25 each for retired members and their spouses. This applies to advance registration only.

On-site registration fees will be $60 full time and $40 one day for members. Non-member fees will be $75 full time and $50 one day. Spouses registration will be $45 on-site.

Registration forms were mailed to all members in April and are included in this issue (see pages 23-27).

Spouses Activities

Included in the spouses registration fee will be a get-acquainted champagne social on Wednesday afternoon; continental breakfast on Thursday and Friday at the Conrad Hilton; and a tour of Chicago with lunch featuring a unique and dazzling show of fashions by Chicago's leading designers.

Federation Luncheon

The Annual Federation Luncheon will be held Friday at the Conrad Hilton Hotel.

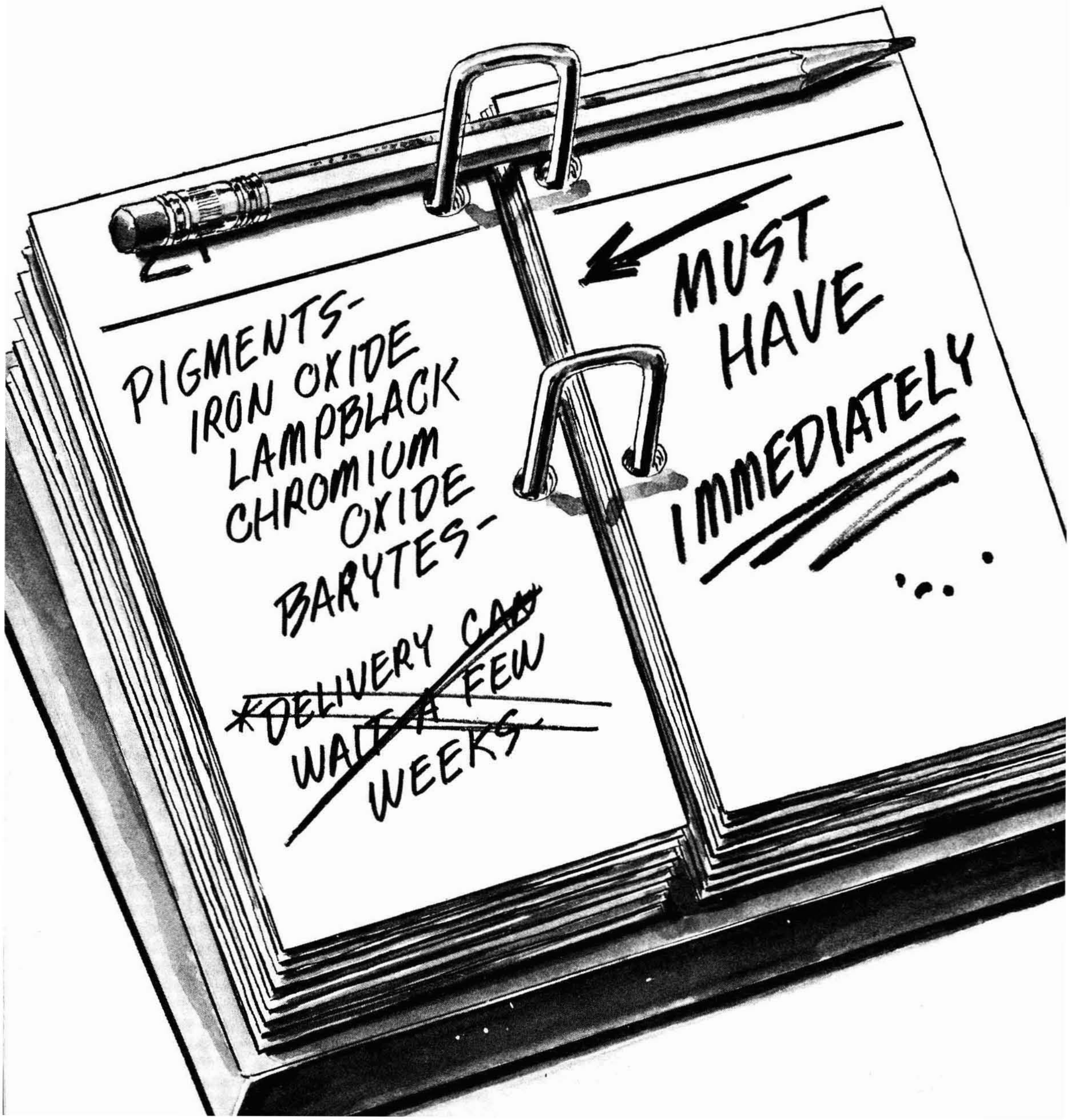
Presentations will be made to the recipients of the George Baugh Heckel Award (outstanding individual who has contributed to the advancement of the Federation) and the Flynn Awards (firms judged to have the best exhibit booths in the 1984 Paint Industries' Show).

Program Committee

Assisting Chairperson Brezinski on the Program Steering Committee are: Joseph A. Vasta (Vice-Chairman), of DuPont Co., Wilmington, DE; Gordon P. Bierwagen, of Sherwin-Williams Co., Chicago, IL; G. Dale Cheever, of General Motors, Warren, MI; Loren Hill, of Monsanto Co., Indian Orchard, MA; Joseph V. Koleske, of Union Carbide Corp., S. Charleston, WV; and Clifford Schoff, of PPG Industries, Inc., Allison Park, PA.

Host Committee

Members of the Chicago Society are serving on the Host Committee under the General Chairmanship of Richard M. Hille, of General Paint and Chemical Co., Cary, IL. Assisting him are: (*Assistant GC and Luncheon*) John T. Vandeberg, of DeSoto, Inc., Des Plaines, IL; (*Program Operations*) Gus W. Leep, of Seymour of Sycamore, Inc., Sycamore, IL; (*Information Services*) Amanda Wentzel, of DeSoto, Inc., Des Plaines, IL; (*FSCT Exhibit*) Victor M. Willis, of Sherwin-Williams Co., Chicago, IL; (*Registration*) Evans Angelos, of Kraft Chemical Co., Inc., Melrose Park, IL; and (*Spouses*) Claudia Hille and Donna Vandeberg.


PIGMENTS-
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MUST HAVE
IMMEDIATELY
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Leidy Chemical • Baltimore, MD (301) 685-2200

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Jensen-Souders • Chicago, IL (312) 773-1830
Matteson-Ridolfi • Detroit, MI (313) 479-4500
Seegott • Cleveland, OH (216) 247-2440

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Walsh & Associates • Memphis, TN (314) 781-2520

WEST-NORTH CENTRAL

Walsh & Associates • St. Louis, MO (314) 781-2520
• Kansas City, MO (816) 842-3014

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Cron Chemical • New Orleans, LA (504) 254-0865
• Houston, TX (713) 644-7561
• Dallas, TX (214) 631-6670

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El Rey Stucco • Albuquerque, NM (505) 873-1180
Walsh & Associates • Denver, CO (303) 295-7696

PACIFIC

Harrison & Crossfield • Seattle, WA (206) 682-4425
• Portland, OR (503) 222-1301
Pfizer • Los Angeles, CA (213) 268-8331

CANADA

Van Waters & Rogers • Toronto (416) 741-9190
(800) 268-0532
• Montreal (514) 631-9451
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Dept. 2C-9 — 235 E. 42nd Street
New York, New York 10017

Coast Guard Buoys Subject of Two-Year Battelle Study

A two-year study to develop improved protective coatings for the U.S. Coast Guard's 48,000 buoys is under way at Battelle's Columbus Laboratories.

The coatings will be used to extend the operation life of salt and fresh water-based buoys, thus reducing costs for their maintenance and replacement. Any improvement to the Aids to Navigation systems is of vital importance to the U.S. Coast Guard, since this mission area commands almost one-third of the Coast Guard's budget.

Recent efforts by the Coast Guard have extended the average life of several components of the buoys to six years, but existing buoy coatings, which prevent corrosion and fouling, cannot meet this six-year standard.

During the study, Battelle will develop and evaluate materials for coating steel, plastic, and aluminum portions of buoys at, and below, the water line. The coatings—intended to provide fouling and corrosion protection while not adversely affecting the marine environment—also must meet stringent abrasion, gouging, and impact-resistance standards.

Battelle paint specialists initially are identifying polymer-based coating candidates for application to buoys. This is being accomplished through extensive review of current data on appropriate coating technology.

Battelle then will apply the best candidates to test panels built of the same structural materials as buoys. The six-by-twelve-inch panels will be immersed in natural seawater at Battelle's Florida Marine Research Facility in Daytona Beach.

The panels will be inspected at six-, twelve-, and eighteen-month intervals to evaluate the coatings' performance and to project the life expectancy they can achieve if used to protect a buoy. Consideration also will be given to coating limitations and use temperature, physical property requirements, and application process needs.

Synthetic Latex Polymer Sales Approach $2 Billion in 1983

U.S. industry consumed over three billion dry pounds of synthetic latex polymers valued at nearly $2 billion in 1983, according to a preliminary report by C.H. Kline & Co., marketing consultants, Fairfield, NJ. These latices, polymerized from monomers emulsified in water, are vital raw materials for the manufacture of a wide assortment of end-use products ranging from paints to paper.

According to Kline, the paint and coating industry, by far the leading consumer, will continue increasing its demand for vinyl-acrylic and acrylic latexes. Government regulations against the use of solvent based paints that emit pollutants have promoted the use of these latexes in interior and exterior house paints, adding further to demand.

Still, merchant polymer suppliers are concerned about the number of paint manufacturers that have backward integrated into the production of their own latexes. On the technical side, a newer generation of latexes, generically called terpolymers, is increasingly being included in paint formulations. Also, considerable work is being done on such specialty applications for paints and coatings as automotive, wire, roofing, floor and deck, and conductive coatings.

Adhesives, the second largest end-use for latex polymers, encompasses a wide range of applications and is perhaps the fastest growing market. This complex market ranges from general purpose glue to structural and engineering adhesives.

Coated and saturated papers provide another major outlet for latex polymers. Although styrene-butadiene is the predominant latex used, such higher performing materials as polyvinyl acelate and its copolymers are making inroads.

Kline indicates the full report will be available in late 1984.

PDCA Names New Director, Charles Holes, At 100th Anniversary Meeting

The Painting and Decorating Contractors of America has named Charles H. Holes to succeed E. Glen Craven as Executive Director effective July 1. The succession was announced this month at the 100th Anniversary Convention of the association.

Mr. Holes, a PDCA staff member since 1974, served most recently as Director of Association Services with major responsibilities in marketing the exhibits at the national convention, and coordinating the national committee activities, the national associate membership program, and the national insurance program. He was also involved in coordinating and promoting the Picture It Painted Professionally (PIPP) program.

He has shared responsibilities for yearbook production, convention planning, and council convention services.

Mr. Craven, who announced his retirement last year, has been Executive Director of PDCA since 1967. Prior to his appointment, he was Executive Secretary of the PDCA Oregon Council. Mr. Craven was Field Organizer for national PDCA and joined the national office as Administrative Assistant to the Executive Director, spending eight years in that position.

H.B. Fuller Coatings Plans Facility Expansion

The Industrial Coatings Div. of H.B. Fuller Co. has announced that it will move into new quarters and expand its Twin Cities operations.

The move to the larger facility in suburban Vadnais Heights, will enable the company to install an additional production line and will provide greater warehouse space for inventory, as well as increased space for research, process engineering, and pilot plant operations.

The company hopes to be fully operational in the new building in June 1984, following structural modifications that will allow the installation of their production equipment.

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY

Housing and Advance Registration Forms

Photo Courtesy of Chicago Convention and Tourism Bureau

62nd ANNUAL MEETING
49th PAINT INDUSTRIES' SHOW

CONRAD HILTON HOTEL • OCTOBER 24, 25, 26

1984 ADVANCE REGISTRATION

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY

1315 Walnut St., Philadelphia, PA 19107

C	Office Use Only
U	Date received ______
	Amount $ ______
V	Check No. ______

Please fill out this form and mail with a check in the correct amount (made payable to the FSCT) to the Federation address shown above. All checks must be payable in U.S. Funds. Any that are not will be returned. DEADLINE DATE FOR ADVANCE REGISTRATION IS SEPTEMBER 17. NONE WILL BE ACCEPTED AFTER THAT DATE.

A $10.00 charge will be made for cancellations received prior to September 17. No refunds will be made after that date.

INDUSTRY REGISTRATION FEES:

A ☐ MEMBER $50.00

Please name the Federation Society in which you are a paid-up member:

______

Federation Constituent Society

B ☐ NON-MEMBER $65.00

G ☐ SPECIAL FEE FOR RETIRED MEMBERS $25.00

______

Federation Constituent Society

INFORMATION FOR REGISTRATION BADGE:

NICKNAME

FIRST NAME LAST NAME

BUSINESS AFFILIATION

STREET

CITY STATE *(U.S. only)*

MAILING ZONE COUNTRY (OTHER THAN U.S.)

BUSINESS CLASSIFICATION DATA FOR THE ABOVE REGISTRANT:

YOUR COMPANY (CHECK ONE BLOCK ONLY)

- AA ☐ Manufacturers of Paints, Varnishes, Lacquers, Printing Inks, Sealants
- BB ☐ Manufacturers of Raw Materials
- CC ☐ Manufacturers of Equipment and Containers
- DD ☐ Sales Agent for Raw Materials and Equipment
- EE ☐ Government Agency
- FF ☐ Research/Testing/Consulting
- GG ☐ Educational Institution/Library
- HH ☐ Paint Consumer
- JJ ☐ Other

YOUR POSITION (CHECK ONE BLOCK ONLY)

- KK ☐ Management/Administration
- LL ☐ Manufacturing and Engineering
- MM ☐ Quality Control
- NN ☐ Research and Development
- PP ☐ Technical Sales Servic
- QQ ☐ Sales and Marketing
- RR ☐ Consultant
- SS ☐ Educator/Student/Librarian
- TT ☐ Other

SPOUSES REGISTRATION AND INFORMATION FOR REGISTRATION BADGE:

D ☐ SPOUSE $35.00

SPECIAL FEE FOR THE SPOUSES OF RETIRED MEMBERS ONLY:
H ☐ $25.00

NICKNAME

NAME

ADDRESS

CITY STATE

MAILING ZONE COUNTRY (OTHER THAN U.S.)

TICKETS FOR FEDERATION LUNCHEON, FRIDAY, OCTOBER 26 (@ $20.00)

Z ☐ NUMBER REQUIRED: ______
$20.00 EACH.

A CHECK IN THE AMOUNT OF:

$ ______

IS ENCLOSED

Federation of Societies for Coatings Technology

YE OLDE PAINT STONE 1737

1984 Annual Meeting
Paint Industries' Show

October 24, 25, 26
Conrad Hilton Hotel
Chicago, Illinois

TO OUR MEMBERS AND FRIENDS:

It is a pleasure for me to invite those associated with the coatings manufacturing industry *everywhere* to the Federation's 62nd Annual Meeting and 49th Paint Industries' Show in Chicago, October 24–26.

These significant coatings events have been held in Chicago more than any other city and we are glad to return after a six-year absence.

The theme of the Program Sessions—"Appearance and Protection—Essential to Our Lifestyle"—recognizes that a thin coating film is the unheralded protector of all surfaces to which it is applied. Dr. Darlene Brezinski directs the Program Committee which is arranging a quality selection of papers, seminars, and other presentations which will address the theme. Speakers will come from throughout the world of coatings science.

The Paint Show grows a little each year and I am proud to say, as have many of my predecessors, that this year's will be the biggest. The exhibit halls of the Conrad Hilton Hotel will be chock full of the traditionally outstanding and colorful exhibits of more than 180 companies.

There will be much to learn and see at the Federation's 1984 big event in Chicago. Please do come.

Terryl Johnson

Terryl Johnson
President
Federation of Societies
for Coatings Technology

FSCT 1984 ANNUAL MEETING AND PAINT INDUSTRIES' SHOW
CONRAD HILTON HOTEL, CHICAGO, ILLINOIS
OCTOBER 24, 25, 26 (Wednesday, Thursday, Friday)

APPLICATION FOR HOTEL ACCOMMODATIONS

MAIL TO:
Fed. Socs. Coatings Tech.
1315 Walnut St.—Dept. H
Philadelphia, PA 19107

Please indicate below the type of accommodations requested and choice of hotels. All reservations will be processed by the Housing Bureau of the Chicago Convention & Visitors Bureau. Hotel assignments will be made in accordance with prevailing availability. The Housing Bureau will send you an acknowledgment, noting the hotel to which you have been assigned. The confirmation of your reservation will come to you directly from the hotel, to whom you must direct all inquiries.

All reservations will be held until 6:00 p.m. and none can be guaranteed after September 28.

TYPE OF ACCOMMODATION	NUMBER	RATE REQUESTED
Single (1 person)		
Double (2 persons)		
Twin (2 persons)		
Suite (parlor and 1 bedroom)		
Suite (parlor and 2 bedrooms)		

CHOICE OF HOTELS:
1st
2nd
3rd
4th

NAMES AND ADDRESSES OF ROOM OCCUPANTS AND DATES OF ARRIVAL/DEPARTURE

Type of Room	Name	Address	Dates Arrive	Dates Depart

Please Type Additional Reservations on a Separate Sheet and Attach to This Form

SEND CONFIRMATION FOR ALL RESERVATIONS TO:

Name ____________________

Company ____________________

Address ____________________

City __________ State or Province __________

Country __________ Mailing Code __________

Telephone __________

Note: Requests for accommodations at the Conrad Hilton will be limited to five rooms per company. A parlor counts as one room.

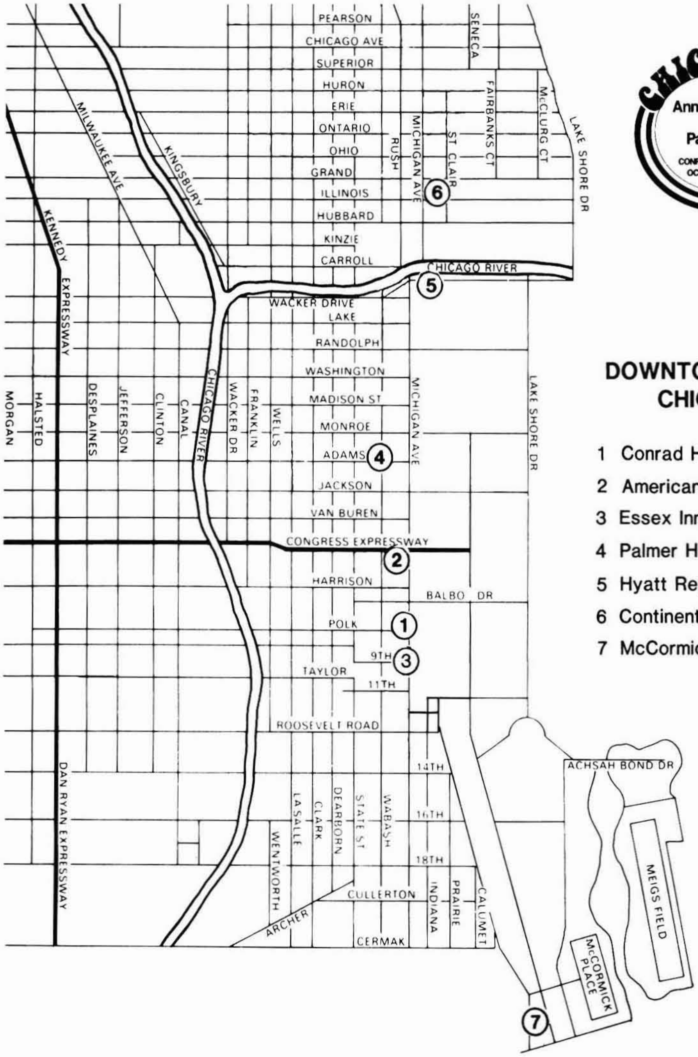
HOTEL INFORMATION AND RATES

All Room Rates Are Subject to a City and State Tax of 9.1%.

Hotel	Singles	Doubles Twin	Parlor & 1 Bedroom	Parlor & 2 Bedrooms
***Conrad Hilton**	65-71-82-86-97	81-97-98-102-113	100 to 355	255 to 475
***Conrad Hilton Towers**	82-102	98-118	"	"
Americana Congress	55	65	85 to 300	175 to 400
Continental	70	85	175 to 240	240 to 450
Essex Inn	46-54-60-66	56-64-70-76		
Hyatt Regency	94-104-114-124	109-119-129-139	175 to 525	275 to 625
McCormick Center	68-78-86-96-104	80-90-98-108-116		
†Palmer House	75-90-105-115-130	95-110-125-135-150	165 &up	395 & up

* Requests for accommodations at the Conrad Hilton will be limited to five rooms per company. A parlor counts as one room. Additional reservations will be assigned to other cooperating hotels.

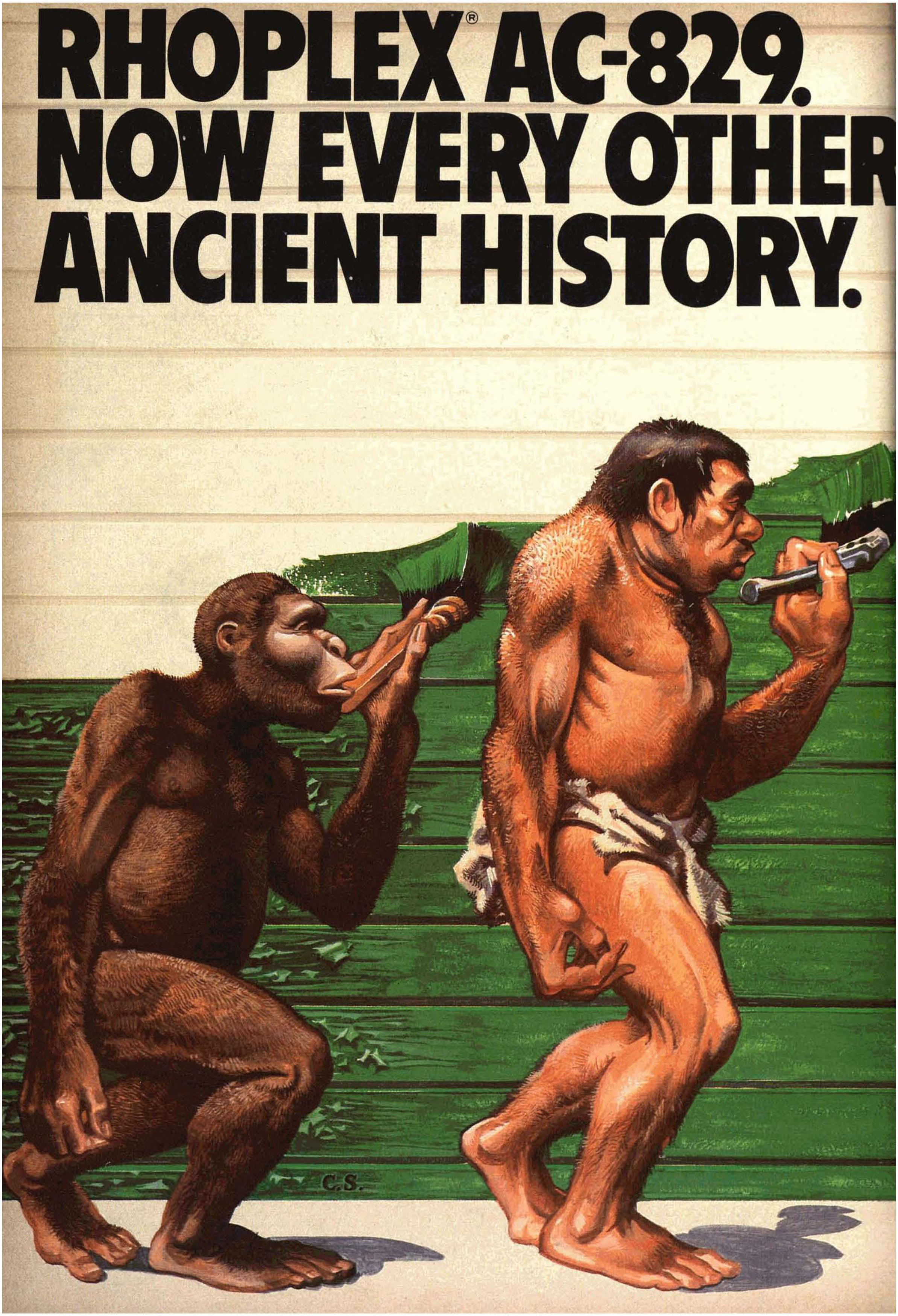
† Reservations for the Palmer House will be accepted for arrival beginning Wednesday only.



CHICAGO '84
FSCT
Annual Meeting
and
Paint Show
CONRAD HILTON HOTEL
OCTOBER 24, 25, 26

DOWNTOWN MAP
CHICAGO

1 Conrad Hilton
2 Americana Congress
3 Essex Inn
4 Palmer House
5 Hyatt Regency Chicago
6 Continental
7 McCormick Inn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NOW EVERY OTHER
ANCIENT HISTORY.
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Cooperative Mildew Research Undertaken by Eight Societies

The Technical Committees of eight Constituent Societies are actively working in the manufacture of experimental paints and the preparation of exterior exposure panels for cooperative research on mildew resistance, and a ninth Society is developing a committee to join in this effort.

As background, about ten years ago the Paint Research Institute provided a research grant to Dr. Charles Pittman, of the University of Alabama, to study the chemistry of attaching fungicides to acrylic monomers. These monomers, when polymerized, might then produce polymers with fungistatic properties. The ultimate objective was to produce polymers which would "fight back" when the paint film was attacked by mildew organisms. The Mildew Consortium of PRI, which was a group of eight companies and organizations formed in 1978, continued to fund Dr. Pittman's work. *(See JCT, April 1978; JCT, July 1982.)*

After a considerable period of time, and based on Dr. Pittman's work, an acrylic monomer to which the fungicide pentachlorophenol had been chemically attached, was produced in larger quantities. From this monomer, one of the Consortium members produced sufficient quantities of an emulsion polymer to permit interested Society Technical Committees to become active in the work. Another member of the Consortium produced stable paints from the "active latex" and made formulation procedures and paint samples available for use by the cooperating Societies.

Enough emulsion polymer was available to allow eight Societies to become involved in manufacturing experimental paints and to prepare panels for exterior exposure. These Societies were asked to make three paints from a formula provided to them, using the "active" and "blank" latex polymers provided by the Consortium.

The paints were to be made as follows:

(1) Paint using the "active" latex polymer (PCP attached chemically to the polymer).

(2) Paint using the "blank" latex polymer (the same acrylic polymer but containing no PCP).

(3) Paint to which a prescribed amount of PCP was incorporated as a stir-in additive.

Exposure panels were to be made from all three experimental paints and placed on exterior racks wherever available to the Society. The Technical Committees were urged to expose panels of commercial mildew-resistant paints along with the experimental paints.

• • •

Following is a brief progress report from the Society Technical Committees presently involved in the cooperative mildew research. Some Societies' involvement began long before others and are thus further along in exposure:

Chicago Society: Paints made and exposure panels prepared. Panels exposed in January 1984 on fences in Wheeling, IL and Homestead, FL.

Golden Gate Society: Collecting raw materials and expect to make paints and prepare panels, Spring 1984.

Kansas City Society: Paints made and exposure panels prepared. Panels exposed in February 1984 in Paola, KS.

Los Angeles Society: Paints made and exposure panels prepared. Panels exposed in July 1983 in the Los Angeles area.

Louisville Society: Paints made and exposure panels prepared. Panels exposed in October 1983 on fences in Homestead, FL.

New England Society: Paints made and exposure panels prepared. Panels exposed in February 1984 on fences in Boston and Puerto Rico.

New York Society: Paints made and exposure panels prepared. Panels exposed in March 1984 on fences in Bayonne, NJ.

Southern Society: Paints made and exposure panels prepared. Panels exposed in October 1983 on fences in Tucker, GA.

Virginia Section—Baltimore Society: Currently organizing a technical committee. Expect to collect raw materials and make paints in Spring 1984.

• • •

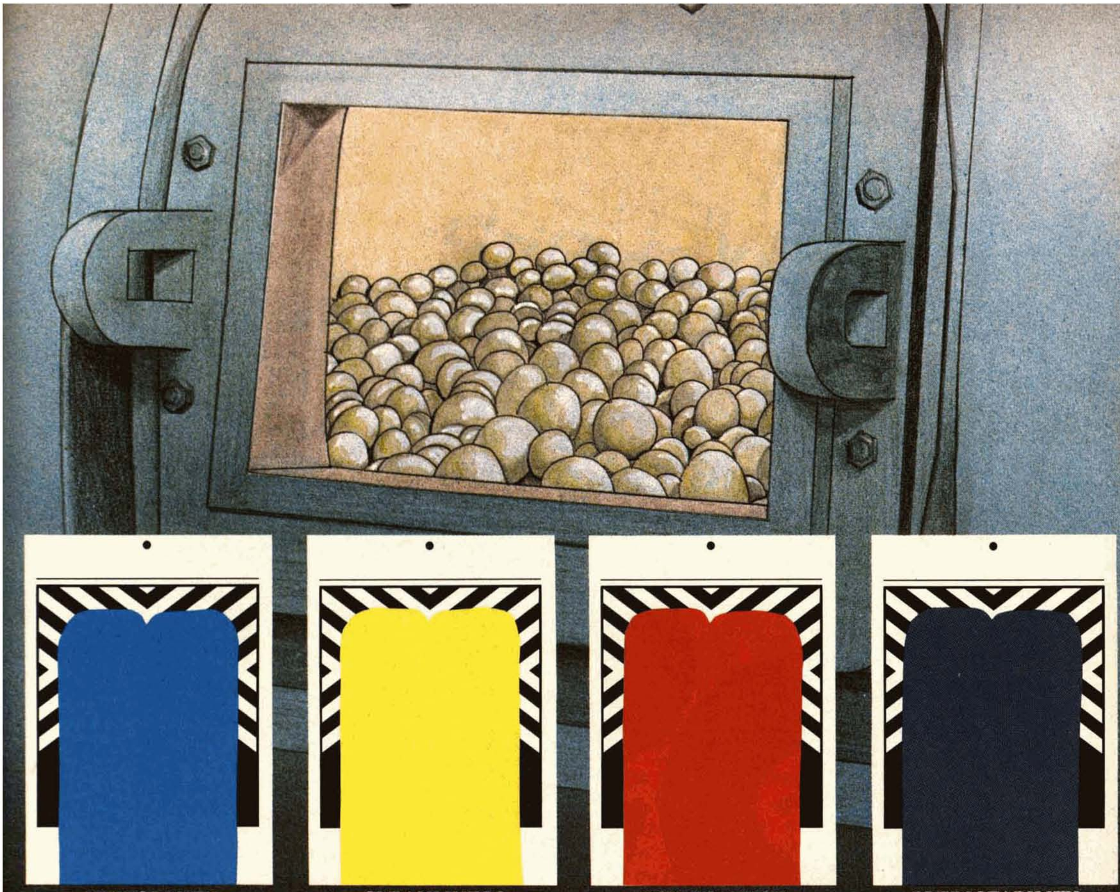
The mildew situation in the United States may be even worse today than previously, now that the effective life of modern exterior paints is longer. A good paint job on a house may last for 5 to 10 years before repainting—if it doesn't mildew in 2 or 3 years.

The discoloration, disfigurement and destruction of exterior painted surfaces by mildew growth is still one of the most troublesome problems encountered by paint manufacturers and users of paint. The addition of mildewcides to exterior paints by the manufacturer helps to retard mildew growth. However, the mildewcide generally leaches from the film and loses its effectiveness in a time period which is considerably shorter than the life of the paint. The paint film, although still protecting the substrate it covers, is then left unprotected and mildew begins to grow.

We believe the idea of a fungicide chemically attached to the polymer offers a promise of success. To be effective the fungicide must be able to hydrolyze and leach out gradually as the paint film weathers. If the fungicide is too tightly bound to the polymer it will probably not control mildew growth. If it is bound too loosely, it will likely leach out rapidly leaving the paint film unprotected.

The best way to determine the effectiveness of a mildew-resistant paint is by exposing panels to the weather against a control as the Societies are doing. This cooperative work is important. Whether the result of their work is positive or negative, the information gained will add to the knowledge necessary to eventually find an effective solution to the mildew problem.

—Royal A. Brown
FSCT Technical Advisor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Protection Of Mildewcides and Fungicides From Ultraviolet Light Induced Photo-oxidation

Peter D. Gabriele and Robert M. Iannucci
CIBA-GEIGY Corporation*

The biological activity of organic and organometallic biocides (fungicides including, mildewcides, antifoulants, pesticides, etc.) can be significantly diminished by photo-oxidation from terrestrial solar radiation. Photo-oxidation reduces biocide efficacy to an extent that a coating service life is lost as a result of biological surface defacement.

The purpose of this study was to determine whether organic and organometallic mildewcides and fungicides can be protected from the effects of ultraviolet photo-oxidation. The methodology demonstrates the protection of mildewcides and fungicides through the use of hydroxyphenyl benzotriazole ultraviolet light absorbers and/or hindered tetraalkyl piperdinol compounds. The evidence developed demonstrates a practical application of a theoretical analysis of mildewcide photo-oxidation. Laboratory analysis and determination of the effectiveness of mildewcide stabilization was accomplished by thin layer chromatography (TLC) and electron capture gas chromatography (ECGC). A simple accelerated laboratory procedure is described for testing and analysis of biocide breakdown and stabilization.

The concept of mildewcide stabilization was additionally supported through a statistical analysis of variance of exterior exposed samples representing all the levels of stabilized formulations compared to all the levels of unstabilized formulations.

Results show that the biological activity of stabilized fungicides and mildewcides in those coatings exposed to terrestrial ultraviolet radiation is maintained when stabilized with hydroxyphenyl benzotriazole and/or a tetraalkyl-piperdinol light stabilizing compound.

INTRODUCTION

The purpose of this study was to investigate protection of the biologically active structure of biocides with hydroxyphenyl benzotriazole and 2,2,6,6-tetramethylpiperdine ultraviolet light stabilizers and their role in the prevention of photo-oxidation.

Organic biocides in coatings (fungicides, which include mildewcides, antifoulants, and algacides) prevent biological surface defacement; however, the gradual and continuous action of ultraviolet solar radiation during service can destroy their biological activity and thus the useful service life of biocides. In short, most organic biocides exposed to sunlight photodegrade.

The ultraviolet portion of the electromagnetic spectrum includes the wavelengths of light between 200 nm and 400 nm. However, the terrestrial solar spectrum includes only those wavelengths longer than 290 nm up to 400 nm. Wavelengths lower than 290 nm are screened out by the ozone layer and upper atmospheres, and thus never reach the earth's surface. Therefore, when photo-oxidation is studied as a component of weathering only those wavelengths longer than 290 nm should be considered. *Figure* 1 shows the relative intensities and cut-off of terrestrial sunlight. Note that the cut-off point is 290 nm.

Biocide activity is rated as a function of the length of time a surface remains mildew free. In addition to photodecomposition, the loss of biocide service life can be attributed to factors including: aqueous leaching, physical migration (acid-rain), hydrolysis, thermal oxidation, polymeric auto-oxidation, microbial decomposition, and generalized formulation incompatibility.

Unlike many of these extrinsic factors, the intrinsic nature and chemical architecture of the biocide molecule directly influence susceptibility to decomposition by sunlight. This condition imposes certain circumstantial limitations to the molecule under direct sunlight performance.

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*Additives Dept., Ardsley, NY 10502.

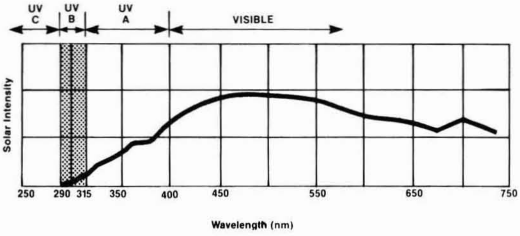


Figure 1—Division and classification of solar UV spectrum

Some biocides can photodecompose and still provide "protection"; however, in a coating, the consequence may be a trade-off in general film appearance. Photo-sensitive biocides can promote film deterioration like chalking, erosion, loss of adhesion, and discoloration. *Figures* 2A and 2B are scanning electron micrographs of two latex coatings after 400 hours exposure in an accelerated weathering device. The coating in *Figure* 2A contains 1% w/w active chlorothalonil. Note the general disruption in film integrity due to the action of UV light. Macroscopically, this coating appears chalky. *Figure* 2B, however, is the same formulation but without chlorothalonil. The general appearance here is uniform as well and the macroscopic appearance is quite like the unexposed control. While the contents of the film in *Figure* 2A may still provide some defacement protection, the coating appearance has lost some aesthetic value.

The photo-oxidation of biocides is well documented[1-3] and in agrochemical treatments is often a required property of the active molecule.[4] However, many biocide applications are intended to provide a prolonged service life as is the case in coatings and wood preservative fungicides. Failure to provide the prolonged protection against biological attack can be directly related to light.[5] *Figure* 3, as an example, demonstrates the variability of performance as a function of exposure direction. In this example, a linseed oil-based stain formulation containing 3-iodo-2-propynl butyl carbamate was applied to two end-matched southern yellow pine boards. Both boards were exposed in New York; one at 45°S, the other at 90°N. After six months exposure the 45°S exposed board was completely defaced with mildew, while the 90°N exposed board was free of mold and mildew. The performance of these samples can be attributed to the action of sunlight decomposition on the biocide.

It is important to note that light initiated oxidation of the biocide is not limited to direct absorption of UV light. In fact, degradation sometimes occurs indirectly as a result of photo-oxidation of other light sensitive components in the coating such as resins, pigments, plasticizers, etc. The free radicals formed from the breakdown of these components can in turn attack UV absorbing as well as non-UV-absorbing molecules which may serve as potential hydrogen donors. Consequently, UV protection of a coating has significant benefit to all film components because of this interdependancy.

Many commercial biocides, however, are characterized by such functional groups as halogens, phosphates, carbamates, aromatic rings, various unsaturated groups,

Figure 2A—Micrograph (1000 X) of latex coating with chlorothlonil following 400 hrs exposure in accelerated weathering device

Figure 2B—Micrograph (1000 X) of latex coating following 400 hours exposure in accelerated weathering device

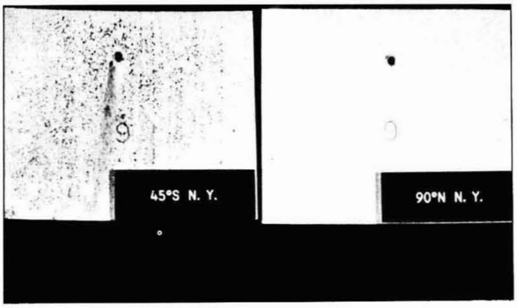
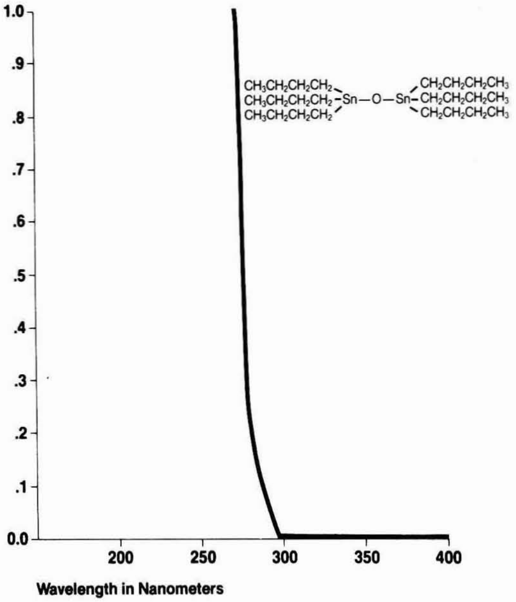


Figure 3—Linseed oil-based stain containing 3-iodo, 2-propynyl carbamate applied to two, end-matched southern yellow pine boards. (Six months' exposure in New York; exposure data shown in lower right corner of boards)

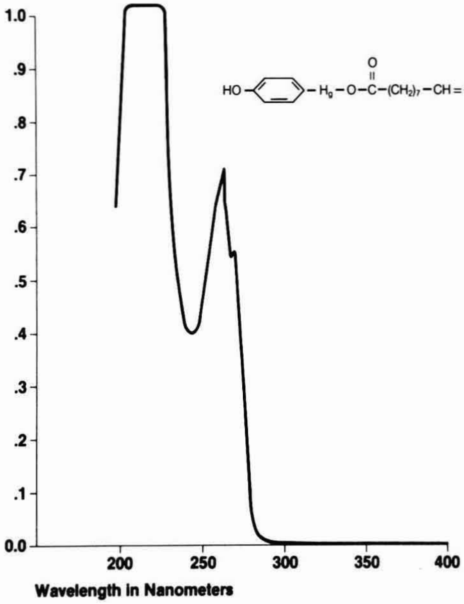
and oxygen containing functional groups. It is the nature of groups such as aromatic rings, ketones, and aldehydes, and their interaction with ultraviolet energy that predisposes most organic biocides toward decomposition.

The toxic activity and thus, the performance of biologically active materials are dictated in part by the specific steric architecture of the active compound. The efficacy and efficiency of a biocide treatment depend upon the maintenance of a minimum inhibitory concentration of the biocide "active" shape during treatment service.[6] This concept is referred to as "shaped charge"; the steric shape of the biocide molecule is necessary to



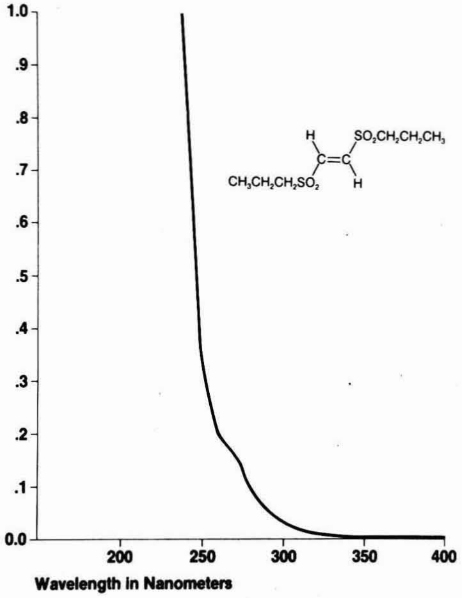
Solvent: CH_2Cl_2
Cell: 1.0 cm.
Concentration: 10 mg./ml.

Figure 4—UV absorbance of tri-butyltin oxide



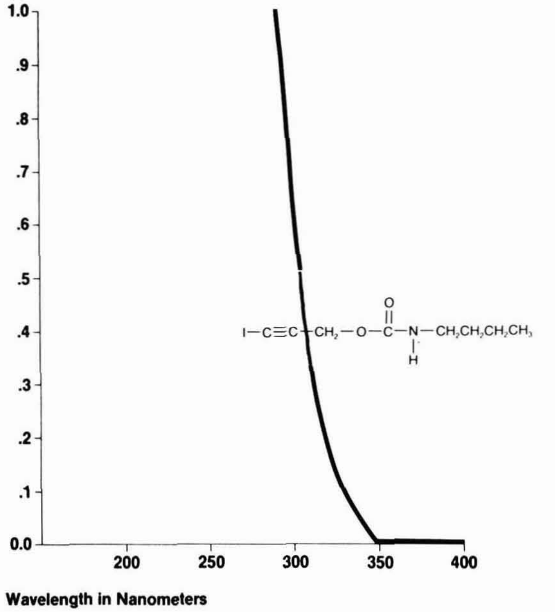
Solvent : Methanol
Cell : 1.0 cm
Concentration : 500 μg/ml

Figure 5—UV absorbance of phenylmercury oleate



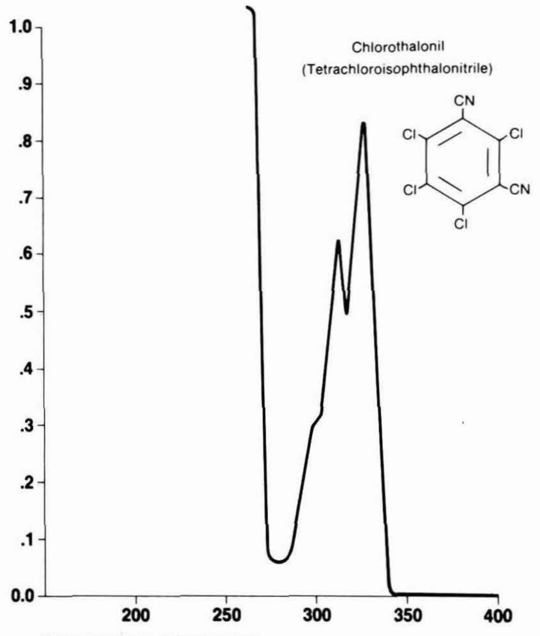
Solvent : Methanol
Cell : 1.0 cm
Concentration : 1 mg/ml

Figure 6—UV absorbance of *trans*-1,2-bis(n-propylsulfonyl)-ethene



Solvent: CH_2Cl_2
Cell: 1.0 cm.
Concentration: 4 mg./ml.

Figure 7—UV absorbance of 3-iodo-2-propynyl butyl carbamate



Solvent: Methanol
Cell: 1.0 cm.
Concentration: 100 µg./ml.

Figure 8—UV absorbance of chlorothalonil

provide toxic activity, regardless of the biocide's particular mode of action.

Natural weathering is a dynamic process of deterioration caused by the interaction of sunlight temperature, oxygen, and moisture. The degree of weathering is additionally influenced by geographic location and seasonal variation in the type and quality of light striking the subject. In addition, the extent of weathering is also a function of the inherent physical and chemical nature of the material. The weatherability of a material can be dramatically affected by excesses of any of these elements, but by far one of the most insidious factors which serves to deliver a lethal blow is natural sunlight.

Photo-oxidation is a natural agent of entropy which promotes the reassimilation of carbon back into the carbon cycle. Radiant energy therefore promotes the destruction and disorder of organic materials. Given enough time, most natural and man-made organic materials subjected to sunlight are likely to decompose. The best we can hope for is to interfere with this entropic process by blocking or checking ultraviolet activity.

Sunlight induced oxidation or photo-oxidation can be simply described as follows (where R represents any polymer, biocide, or other coating compound capable of absorbing UV light):

$$\overset{\text{UV Radiation}}{\downarrow} \quad R \xrightarrow{\text{Step 1}} R^{*} \xrightarrow{\text{Step 2}} R\bullet \xrightarrow{\text{Step 3}} \text{Degradation}$$

Step 4

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

Step 5

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \qquad (1)$$

$$ROOH \xrightarrow[\text{Step 6}]{\text{UV Radiation}\downarrow} RO\bullet + \bullet OH$$

Light may be absorbed by a number of components within a coating. The absorption of ultraviolet energy by the coating system is a necessary first step in the photo-oxidation process (Step 1). Following the absorption of UV light, the system is said to be raised to a higher, less stable energy state referred to as the excited state (R*). This excited state is a condition in which the molecular orbital geometry of the system is distorted because of the excess absorbed energy within the electron cloud. Excited state molecules are very reactive and may undergo a wide range of processes to accommodate this energy. If the molecule is unable to adjust to this excess in energy, bonds may dissociate (Step 2). A common dissociation is in the form of a free radical (R ·), usually a highly reactive chemical species which contains an unshared electron. The formation of a radical marks a dramatic change in the chemical nature of the molecule.[7]

The process of degradation can continue beyond radical formation. Radicals can combine with oxygen and initiate the further process of auto-oxidation (Steps 4–6). The free radical combines with oxygen to form a peroxy radical (Step 4), which in turn may abstract hydrogen from an available donor resulting in the formation of polymeric hydroperoxide (Step 5). The result is a destruction of the integrity of the chemical environment. One free radical can form literally thousands of polymeric hydroperoxide species and thus, the rapid promotion of degradation.

Figures 4 through 9 are formulae and UV spectra of many of the commercial fungicides used to prevent mildew defacement. Numerous UV sensitive functional groups within these molecules allow them to absorb UV light. Any absorption of wavelengths longer than 290 nm is often an indicator that the molecule will be susceptible to photodegradation. One exception to this is Tri-butyl Tin Oxide, which is unstable despite its low absorbance above 290 nm. Another example is trans-1,2-bis(n-propylsulfonyl)ethene. Under this circumstance, it is more likely that these materials decompose through either a radical attack or auto-oxidation process as a result of a contaminant or other photosensitive material in the environment.

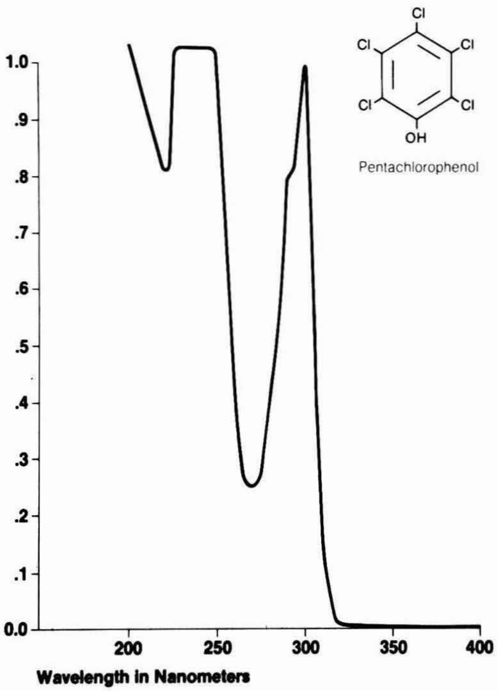
Light stabilizers are chemical additives used at low levels which impede photodegradation and thus, extend the useful service life of a coating or plastic. Different classes of light stabilizers operate by different mechanisms to slow degradation. Classic ultraviolet absorbers (UVA) are one class of chemicals with strong absorptivity in the ultraviolet range (see *Figure* 10), but with the special capability of dissipating the absorbed energy harmlessly without compromising the UVA molecule.[8,9] In contrast, many biocide molecules also have good ultraviolet absorptivity but are unfortunately destroyed for lack of an effective mechanism to dissipate excess absorbed radiant energy.

A relatively new class of stabilizers known as the hindered amine light stabilizer (HALS) does not act by UV absorption, but rather operates by a completely different mechanism.[10,11] The most widely accepted theory of HALS activity involves radical termination. Therefore, combining a UVA with a HALS can check the photodegradation process in two levels (See Equation 1, Steps 1 and 2). It is not unusual for combinations of light stabilizers to increase the service life of a coating by acting synergistically.

It is with these concepts of UV stabilization that we began our study. As a multicomponent system, a coating may promote mildew defacement in a number of ways. In addition to a photosensitive biocide, the coating may contain nutritional components from such raw materials as oils, surfactants, thickeners, etc., which microorganisms may use as a source of carbon for nutrition, and, therefore, promote defacement.

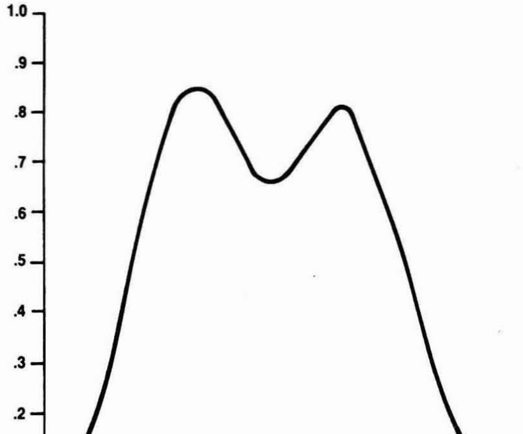
The evaluation of the biocide photo-oxidation process can only be studied clearly if biocide degradation can be identified and isolated. Indirect methods such as ASTM 3274[12] do not isolate this process precisely. This is because the assessment involves the response of a biological system as a mode of evaluation. The biological system itself is chemically more complex and adaptable than the system under study.

Because of the complexity of biocide degradation, we approached this study in several ways. Our initial investigation began with model studies of stabilized and



Solvent: CH_2Cl_2
Cell: 1.0 cm
Concentration: 0.1 mg/ml

Figure 9—UV absorbance of pentachlorophenol



Solvent: Chloroform
Cell: 1.0 cm.
Concentration: 2.0 mg./100 ml.

Figure 10—UV absorbance of 2(2,hydroxy-3′,5′-di-tert-amyl-phenyl)benzotriazole

Table 1—Fungicide/Mildewcide Classification[a]

Fungicide	Tradename	Manufacturer	Commercial Uses
Organic Sulfur			
Trans-1,2-Bis(n-propylsulfonyl)ethene	Vancide® PA	R.T. Vanderbilt Co.	Mildewcide
Organometallic			
Bis-tri-n-butyl tin oxide	TBTO®	M&T Chemical, Inc.	Wood preservative
Phenyl mercury oleate	PMO®-30	Troy Chemical Corp.	Mildewcide/preservative
Aromatics			
Chlorothalonil	Nopcocide® N-96	Diamond-Shamrock Corp.	Mildewcide
Non-aromatic Organic			
3-Iodo-2-propyl butyl carbamate	Polyphase®	Troy Chemical Corp.	Mildewcide/Wood preservative

(a) Classification described in "Fungicides, Vol. II, Chemistry and Physiology," D. C. Torgeson, Academic Press, New York.

unstabilized chlorothalonil solutions exposed to artificial UV light. Following exposure, these solutions were analyzed by electron capture gas chromatography (ECGC) for the percent remaining chlorothalonil. We soon recognized that solution dynamics were significantly different than film dynamics.

As a result, we developed an improved laboratory exposure model to screen, identify, and isolate biocide performance such that we could directly evaluate the remaining active biocide in a film. The improved system was designed to hold the biocide in a clear acrylic film matrix coated onto the interior wall of a borosilicate vial so as to confine the film and degradants. Following exposure, the vial films were extracted off the vial and their contents analyzed by Thin Layer Chromatography (TLC).

Finally, our study was concluded with an outdoor exposure of two biocides: one a UV active material, the other somewhat less active. In both cases, and especially in the outdoor results, we have demonstrated protection of the biocide and extension of service life using ultraviolet light absorbers in combination with hindered amine light stabilizers.

A statistical analysis of variance of mean mildew ratings of the outdoor exposure was performed after six months. Variance analysis of samples indicate that stabilized biocide formulations resisted mildew attack significantly more than unstabilized samples.

Furthermore, examination of mildew ratings for a 12-month period indicate that linseed oil-based stains, containing 0.5% mildewcide and stabilized with a combination of 1-2% hydroxyphenyl benzotriazole and 1% hindered amine, performed equal to or better than unstabilized stains, containing higher levels of mildewcide (Stabilizer concentrations are based on the percentage of total resin solids; biocide concentrations are based on total formulation weight). Thus, the result of stabilization of 0.5% 3-iodo-2-propyl butyl carbamate and 0.5% trans-1,2-bis(n-propylsulfonyl)ethene was a four-fold extension in activity and roughly the same mildew-free surface rating as their respective 2% unstabilized mildewcide levels. Stain samples containing no mildewcide but containing equivalent levels of stabilizers as in stabilized stains containing mildewcides, did not prevent mildew growth. Therefore, light stabilizers were determined not to have biological activity.

These results suggest that resistance of mildew attack was mainly the result of biocide protection by light stabilizers.

Materials are listed in *Tables* 1, 2, and 3.

Table 2—Stabilizer Classification

Stabilizer	Chemical Name	Tradename	Designation
Benzotriazole	2(2-hydroxy-3′,5′-di-tert-amylphenyl benzotriazole)	Tinuvin® 328[a]	UVA 1
Hindered amine	Bis(1,2,2,6,6-pentamethyl-4-piperdinyl)[3,5-bis(1,1-dimethyl-4-hydroxyphenyl)methyl]butyl propanedioate	Tinuvin® 144	HALS 1
	Proprietary structure		HALS 2
	Bis(1,2,2,6,6-pentamethyl-4-piperdinyl)sebacate	Tinuvin® 292	HALS 3

(a) Tinuvin is the tradename of CIBA-GEIGY light stabilizers, Ardsley, NY.

METHODS

Laboratory Models

SOLUTION STUDY: As a preliminary study into biocide photo-oxidation, stabilized and unstabilized chlorothalonil solutions in toluene were periodically exposed to UV light (FS/BL). Following exposure, solutions were analyzed by electron capture gas chromatography (ECGC) for the percent remaining biocide.[13]

The efficiency of molecular absorption is characterized by the extinction co-efficient ϵ. It is a constant that describes the intrinsic light absorbing characteristic of a molecule at a specific wavelength of light. The extinction co-efficient is determined from the UV spectra of the absorbing molecule using Beer's law:

$$O.D. = A = \epsilon\, CL;\ \text{therefore;}$$

$$\epsilon = \frac{A}{CL} \quad ;\ \text{where}$$

O.D. = optical density
A = absorbance value
C = Concentration in moles/liter
L = path length of light through the sample (1.0 cm)
ϵ = the extinction co-efficient (liters/mole·cm)

Once the extinction constant is determined, the Beer's law formula can be manipulated to calculate the corresponding value of concentration for any theoretically assigned absorbance value (A) or optical density (O.D.) since absorbance is proportional to concentration:

$$C^{UVA1} = \frac{A^{UVA1}_{313}}{\epsilon^{UVA}_{313}\, L}$$

or

$$C_{Biocide} = \frac{A^{Biocide}_{313}}{\epsilon^{Biocide}_{313}\, L}$$

In this study, UVA 1 and chlorothalonil were combined in solution such that the calculated concentration of UVA 1 gave a theoretical absorbance (A) or optical density (O.D.) value of 3.0; while the corresponding concentration of chlorothalonil was calculated to give a value of 1.0. Thus, in solution the absorbance ratio of UVA 1 to chlorothalonil was 3:1. Both concentration values were calculated from their respective extinction co-efficients at 313 nm, since this is approximately an absorbance maximum common to both the UVA 1 and chlorothalonil molecules. The ratio relationship is described as follows:

$$\frac{O.D.^{UVA1}_{313}}{O.D.^{Biocide}_{313}} = \frac{A^{UVA1}_{313}}{A^{Biocide}_{313}} = \frac{\epsilon^{UVA1}_{313}\, CL}{\epsilon^{Biocide}_{313}\, CL} = \frac{3.0}{1.0}$$

where;

$O.D._{313}$ = the optical density of the absorbing molecule at 313 nM UV light
A_{313} = the absorbance value of the absorbing molecule light (A_{313} = O.D.313)
ϵ_{313} = the extinction co-efficient of the absorbing molecule at 313 nM UV light
C = the concentration of the absorbing molecule in moles/liter
L = the pathlength of light through the sample (1.0 cm)

Since HALS do not absorb UV light, absorbance ratioing is impossible. Therefore, an arbitrary concentration value of 100 μg/mL was chosen.

Table 3—Additional Materials

QUV Accelerated Weathering of Device — Q Panel Co.
Fluorescent Sunlight/Blacklight Exposure Device (American Cyanamid Bulletin)
  Black Light Source—Sylvania F40BL
  Sun Lamp Source—Westinghouse FS40
20 mil Kimble Scintillation Vials KIM-74500
Merck TLC Plates Silica Gel 60F-254
Rohm and Haas Acryloid® B-66
Toluene Spectro MCBTX-740
20 mil Kimax Borosilicate Test Tube
Permeable Membrane Cap Closures Fischer 14-957
KC18 "Reverse Phase" TLC Plate

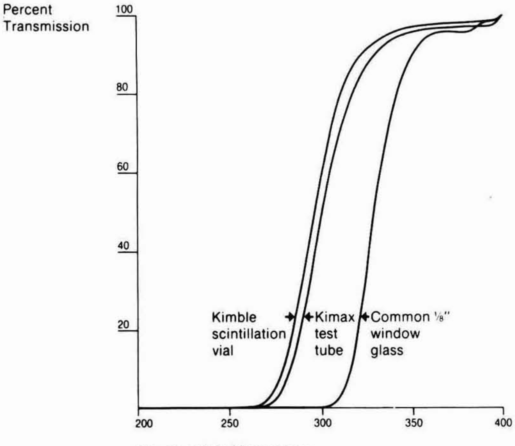


Figure 11—Comparison of the UV transmission of common window glass and Kimax scintillation and test tube glass

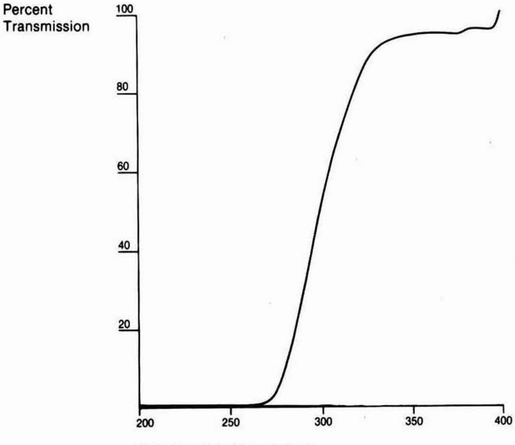


Figure 12—Kimax scintillation vial with blank acylic matrix coating on interior wall

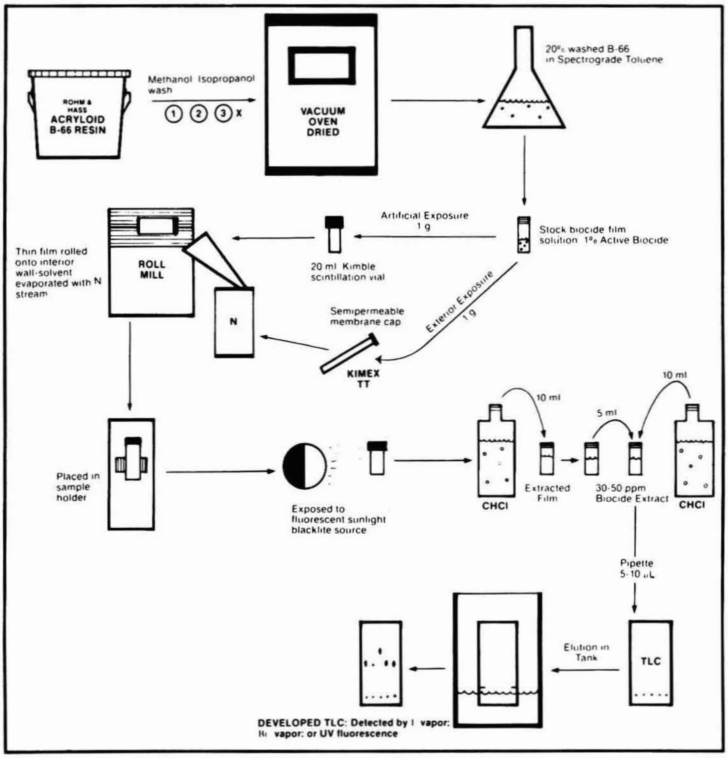


Figure 13—Flow diagram for thermoplastic acrylic film model preparation

Chlorothalonil solutions were prepared as follows:

(1) 20 μg/mL Chlorothalonil in toluene.
(2) 20 μg/mL Chlorothalonil + 75 ppm UVA 1 in toluene.
(3) 20 μg/mL Chlorothalonil + 100 ppm HALS 1 in toluene.

The above fungicide solutions were pipetted into borosilicate Kimble scintillation vials, capped, and labeled to indicate the amount of time exposed. All samples were exposed in a fluorescent sunlight/blacklight box (FS/BL). Samples from each solution were retrieved at 0, 10, 20, and 30 minute intervals of exposure and analyzed by electron capture gas chromatography (ECGC). Data points for each time interval represent a run of three samples per exposure time interval.

A transmission spectra of a piece of the glass from a scintillation vial was obtained. The spectra (*Figure* 11) demonstrated excellent transmission of UV light longer than 290 nm and <5% shorter than 280 nm indicating the vial was an "open window" to terrestrial UV radiation wavelengths.

THERMOPLASTIC ACRYLIC FILM MODEL/THIN LAYER CHROMATOGRAPHY ANALYSIS: *Extraction and Thin Layer Chromatography (TLC)*—Although the solution study was able to demonstrate the usefulness of light stabilizers, it was obvious that solution dynamics are considerably different from film dynamics. To apply the stabilization concept to coatings science, a thermoplastic acrylic ester film model was developed which would (1) place the biocide in a chemical and physical environment that closely approximates film dynamics; and (2) provide a simplified film system to contain only those variables under study, thereby minimizing film component interactions, confining breakdown products for study, and eliminating any variability of adaptive growth by defacement organisms.

A 15% solution of a thermoplastic acrylic ester resin was prepared in toluene following several successive washings of the B-66 acrylic in methanol/isopropanol (1:1) to remove processing contaminants. The washed resin was vacuum dried to within a few percent of the original dry weight before the final 15% acrylic solution in toluene was prepared.

Stock acrylic/biocide wet formulations were prepared for each biocide in combination with various light stabilizer additives. The biocide composition of each formulation was 1.0% active biocide on the total formulation weight. Light stabilizer additions were also added based on total formula weight in this test.

One gram of each stock formulation was roll coated into separate Kimble 20 mL scintillation vials to a thin film onto the interior wall, dried by evaporation in a nitrogen stream, capped closed, and exposed in a FS/BL Weatherometer® for various exposure times. *Figure* 12 shows a transmission spectra of the acrylic control vial. This spectra demonstrates the lack of UV absorption by the model matrix.

Following exposure, 10 mL of chloroform was introduced into each vial to extract the film in the interior wall.

Table 4—TLC Systems of Biocide Exposed in Acrylic Film

Fungicide	Solvent System	Detection
3-Iodo-2-propyl butyl carbamate	Methylene chloride/Methanol 98:2 (FS/BL) Hexane/Acetic acid 80:20 (exterior)	Iodination and UV fluorescence
Chlorothalonil	Methylene chloride (FS/BL) Hexane/Acetic acid 80:20 (exterior)	UV fluorescence
Pentachlorophenol	Methylene chloride/Methanol 90:10 (FS/BL) Hexane/Acetic acid 80:20 (exterior)	UV fluorescence
TBTO	Hexane/Acetic acid 80:20	Bromination and subsequent staining with pyrocatechol violet
PMO-30[a]	Acetonitrile/Water 95:5	Staining with dithizone

(a) Partitioning using KC18 "Reverse Phase" TLC plate.

A 5 mL aliquot of the extraction was further diluted in an additional 10.0 mL of chloroform and a TLC performed on precoated TLC Silica Gel Plates 60F-254 (Merck). The spot applied to the origin of each TLC had a biocide concentration of approximately 3 to 5 ppm. This procedure is illustrated in a flow diagram, *Figure* 13.

The duration of exposure for each film/biocide sample was established in preliminary experiments. Using only the neat unstabilized biocide/films, a number of film models per neat biocide were exposed to ultraviolet light (FS/BL) and periodically retrieved for TLC analysis. Our final test exposure times were established when the neat biocide R_f value had disappeared or had significantly changed.

The basis of determining effective stabilization was, therefore, the comparative retention of R_f values of the exposed/stabilized biocide/film TLCs to that of the unexposed/unstabilized and exposed/unstabilized control films (see *Table* 4). All unexposed/unstabilized sample controls were stored in the dark during the period in which exposed samples were subjected to UV radiation.

Exterior Exposure

A white linseed oil based solid stain was formulated using mildewcide levels from 0.25% to 2.5% w/w in combination with a UVA, a UVA and HALS 3, or a HALS 3 alone. The following stabilizer levels were tested based on resin solids of 22%:

(1) 1.0% hydroxyphenyl benzotriazole (UVA 1)
(2) 1.0% tetramethylpiperdine (HALS 3)
(3) 1.0% hydroxyphenyl benzotriazole and 1.0% tetramethylpiperdine (UVA 1) + (HALS 3)
(4) 2.0% hydroxyphenyl benzotriazole and 1.0% tetramethylpiperdine (UVA 1) + (HALS 3)

Stains were applied to Southern Yellow Pine boards. End-matched board samples of each formulation and controls were exposed at both 45° S and 90° N in Ardsley, NY. Test samples were weathered for 12 months.

The two mildewcides examined were:

(1) *Mildewcide 1* (3-iodo-2-propynlbutylcarbamate)
(2) *Mildewcide 2* (trans-1,2-bis(n propylsulfonyl)ethene

The performance of each mildewcide was observed to vary with concentration. Also observed were the inherent performance differences between fungicide products.

The effectiveness of light stabilization of the mildewcide was determined as the ability of the coating to prevent mildew defacement of the coating surface as a function of time. Mildew defacement was rated according to ASTM D3274-76. Mildew defacement of the coating was rated

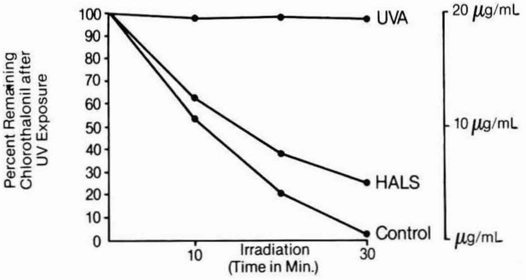
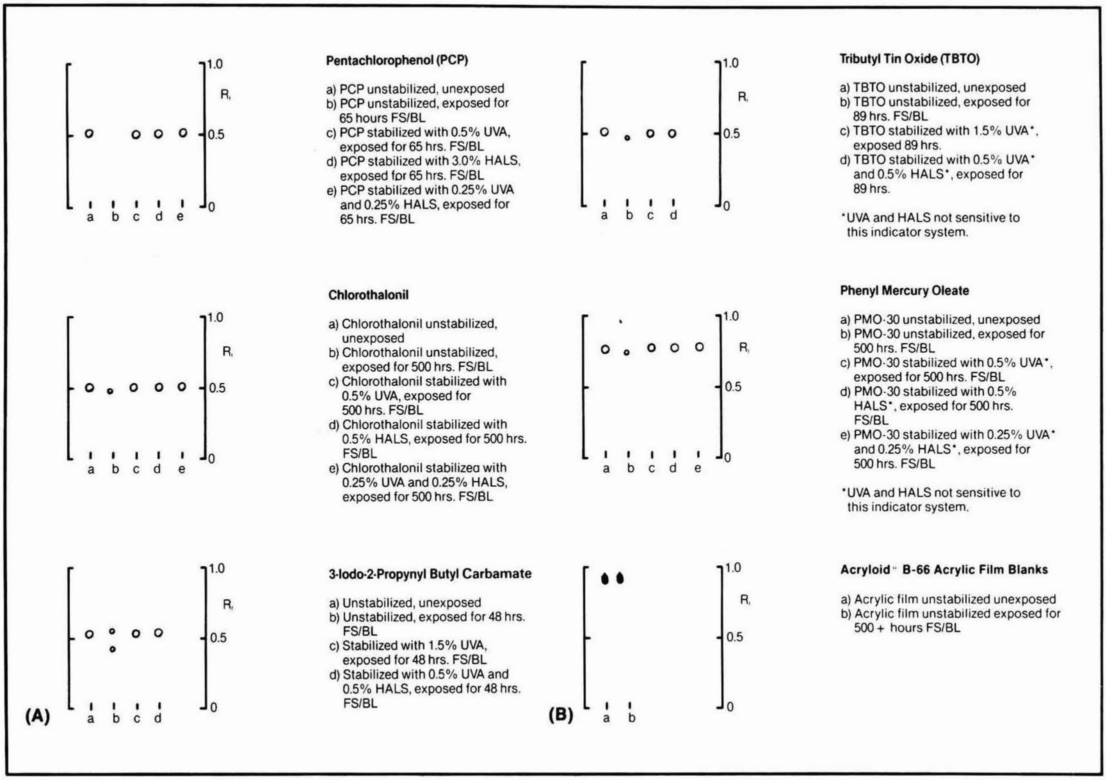


Figure 14—Electron capture gas chromatography analysis of % remaining chlorothalonil in toluene solution after UV exposure in FS/BL fluorescent sunlight/black lightbox. (Each point represents an average of three test runs)

Table 5—Breakdown Times of Each Biocide Exposed In the Acrylic Films

Biocide	Time Required For Total Photo-decomposition (hr FS/BL)
3-Iodo-2-propynl butyl carbamate	48
Chlorothalonil	500
Pentachlorophenol	65
Tri-n-butyl tin oxide	89
Phenyl mercury oleate	500
Trans-1,2-bis(n-propylsulfonyl)-ethene	No breakdown



Pentachlorophenol (PCP)

a) PCP unstabilized, unexposed
b) PCP unstabilized, exposed for 65 hours FS/BL
c) PCP stabilized with 0.5% UVA, exposed for 65 hrs. FS/BL
d) PCP stabilized with 3.0% HALS, exposed for 65 hrs. FS/BL
e) PCP stabilized with 0.25% UVA and 0.25% HALS, exposed for 65 hrs. FS/BL

Chlorothalonil

a) Chlorothalonil unstabilized, unexposed
b) Chlorothalonil unstabilized, exposed for 500 hrs. FS/BL
c) Chlorothalonil stabilized with 0.5% UVA, exposed for 500 hrs. FS/BL
d) Chlorothalonil stabilized with 0.5% HALS, exposed for 500 hrs. FS/BL
e) Chlorothalonil stabilized with 0.25% UVA and 0.25% HALS, exposed for 500 hrs. FS/BL

3-Iodo-2-Propynyl Butyl Carbamate

a) Unstabilized, unexposed
b) Unstabilized, exposed for 48 hrs. FS/BL
c) Stabilized with 1.5% UVA, exposed for 48 hrs. FS/BL
d) Stabilized with 0.5% UVA and 0.5% HALS, exposed for 48 hrs. FS/BL

Tributyl Tin Oxide (TBTO)

a) TBTO unstabilized, unexposed
b) TBTO unstabilized, exposed for 89 hrs. FS/BL
c) TBTO stabilized with 1.5% UVA*, exposed 89 hrs.
d) TBTO stabilized with 0.5% UVA* and 0.5% HALS*, exposed for 89 hrs.

*UVA and HALS not sensitive to this indicator system.

Phenyl Mercury Oleate

a) PMO-30 unstabilized, unexposed
b) PMO-30 unstabilized, exposed for 500 hrs. FS/BL
c) PMO-30 stabilized with 0.5% UVA*, exposed for 500 hrs. FS/BL
d) PMO-30 stabilized with 0.5% HALS*, exposed for 500 hrs. FS/BL
e) PMO-30 stabilized with 0.25% UVA* and 0.25% HALS*, exposed for 500 hrs. FS/BL

*UVA and HALS not sensitive to this indicator system.

Acryloid® B-66 Acrylic Film Blanks

a) Acrylic film unstabilized unexposed
b) Acrylic film unstabilized exposed for 500 + hours FS/BL

Figure 15 A-B—TLC composite of analyzied acrylic/biocide film model after FS/BL exposure

on a scale of 1-10. A top scale 10 rating represented a clear mildewfree surface, whereas, a 1 rating represented total defacement.

At six months, a statistical analysis of variance was performed on all the mildew ratings of all the levels of mildewcide. This represented a total of 136 samples rated for the comparison of all levels of unstabilized mildew values to all the levels of stabilized mildewcides for all levels of mildewcides tested.

RESULTS

Laboratory Models

SOLUTION STUDY: Analysis of the exposed fungicide solutions showed a 98% loss of chlorothalonil within 30 minutes of exposure (see *Figure* 14).

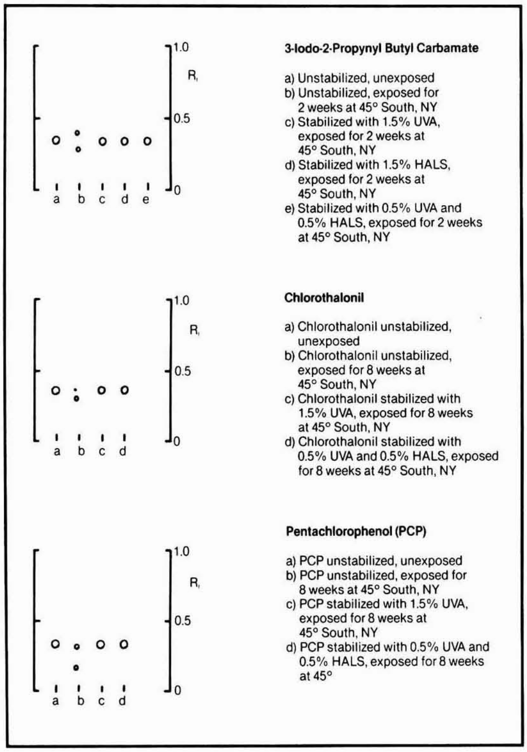
The addition of the UVA significantly affected the percent remaining chlorothalonil after exposure. After 30 minutes exposure, 97% of the UVA stabilized chlorothalonil remained as opposed to only 2% in the control. Following 60 minutes exposure, UVA protected chlorothalonil showed 86% remaining.

The hindered amine light stabilizers were not expected to perform as well as the UVA in this experiment since HALS do not act as UV absorbers. The most significant improvement with HALS was 25% chlorothalonil remaining, stabilized with HALS 1, compared to less than 2% in the control.

Under the conditions of this test, a UV absorber was the optimal stabilizer for protection. Solutions containing the combination of stabilizers did as well as the UV absorber alone, indicating that the major protecting agent in the combinations was the UVA for this accelerated solution study. Field test conditions, which include a greater number of variables, show the combination to possess superior performance.

THERMOPLASTIC ACRYLIC FILM/BIOCIDE MODEL: *Extraction and Thin Layer Chromatography (TLC)—Table* 5 shows the respective breakdown times of each biocide represented in this film test. The relative breakdown times of these biocides should not be extrapolated to actual field performance, which depends on a variety of additional factors.

Figures 15A, 15B, and 15C illustrate TLC results of unstabilized and stabilized biocides extracted from the acrylic films exposed in the FS/BL. Each chromatogram represents the comparative R_f values of the unstabilized biocide to the stabilized biocide. Accordingly, the first two spots represent the unstabilized/unexposed and unstabilized/exposed controls, respectively. Spots representing stabilized biocides occur adjacent to the controls. In addition to biocide/films exposed to artificial radiation, a modification of the model was developed for



3-Iodo-2-Propynyl Butyl Carbamate

a) Unstabilized, unexposed
b) Unstabilized, exposed for 2 weeks at 45° South, NY
c) Stabilized with 1.5% UVA, exposed for 2 weeks at 45° South, NY
d) Stabilized with 1.5% HALS, exposed for 2 weeks at 45° South, NY
e) Stabilized with 0.5% UVA and 0.5% HALS, exposed for 2 weeks at 45° South, NY

Chlorothalonil

a) Chlorothalonil unstabilized, unexposed
b) Chlorothalonil unstabilized, exposed for 8 weeks at 45° South, NY
c) Chlorothalonil stabilized with 1.5% UVA, exposed for 8 weeks at 45° South, NY
d) Chlorothalonil stabilized with 0.5% UVA and 0.5% HALS, exposed for 8 weeks at 45° South, NY

Pentachlorophenol (PCP)

a) PCP unstabilized, unexposed
b) PCP unstabilized, exposed for 8 weeks at 45° South, NY
c) PCP stabilized with 1.5% UVA, exposed for 8 weeks at 45° South, NY
d) PCP stabilized with 0.5% UVA and 0.5% HALS, exposed for 8 weeks at 45°

Figure 15 C—TLC composite of analyzed acrylic/biocide film after exterior exposure

exterior exposure. Substitution of a borosilicate Kimble test-tube for the glass vial, and replacement of the common plastic caps with 0.45 μ polyethylene semi-permeable membrane caps, provided a test-tube version of the model to evaluate films under outdoor natural sunlight. With the semi-permeable membrane, the films were exposed to natural atmospheric conditions without biological contamination.

We interpret these TLC data (*Figures* 15A, 15B, and 15C) to indicate that the biocide molecule has been kept intact when stabilized.

Exterior Exposure Results

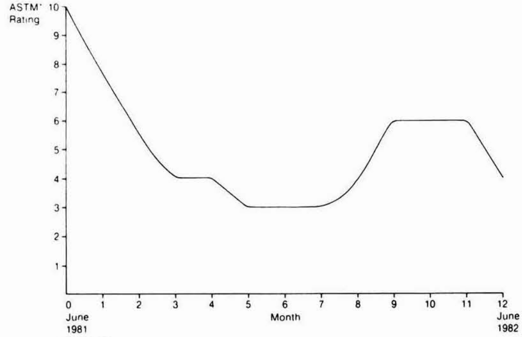
All coating samples were exposed in Ardsley, NY. The control samples exposed at 45° South (unstabilized mildewcides) began to severly fail between months 4 and 5 with a mildew rating of 5 or less. In all cases, 45° South Ardsley exposed samples began to fail 13 months before the 90° North samples. This indicates the role UV light plays in fungicide performance and demonstrates the influence of direct sunlight and orientation on mildewcide "weatherability."

The effectiveness of light stabilization varied with fungicide concentration. The benefit of stabilization was best demonstrated at the 0.5% mildewcide concentration. Stabilized mildewcides, 3-iodo-2-propynl butyl carbamate and trans-1,2-bis(n-propylsulfonyl)ethene showed performance equal to or better than higher concentrations of their unstabilized controls.

Below the 0.5% level, the amount of mildewcide was probably not sufficient to provide defacement protection in this exposed environment. Below the 2% biocide level, performance was initially good but degenerated with time. At the 2% level the systems held up rather well (ratings > 7) probably due to a maintenance of a MIC even with biocide degradation.

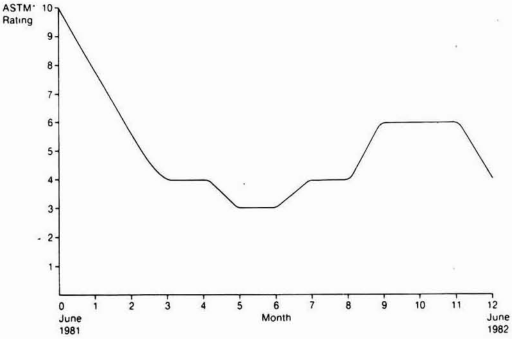
Both 3-iodo-2 propyl butyl carbamate and trans-1,2-bis(n-propylsulfonyl) ethene when stabilized with a combination of 2% UVA + 1% HALS 3, or 1% UVA + 1% HALS 3 gave the most consistent performance over 12 months (see *Figures* 20 and 21).

These stabilized samples of 3-iodo-2-propynl butyl carbamate and trans 1,2-bis(n-propylsulfonyl)ethene after 12 months exposure, had the same mildew ratings as their respective unstabilized controls at three months, giving 3-iodo-2-propynl butyl carbamate and trans-1,2-bis(n-propyl-sulfonyl)ethene a four-fold extension in service and roughly the same mildew free surface rating as their 2% unstabilized mildewcide levels.



*D3274-76

Figure 16—Relative mildewcidal activity of light stabilizer combinations (0% mildewcide with paraffin; no light stabilizer)



*D3274-76

Figure 17—Relative mildewcidal activity of light stabilizer combinations (0% mildewcide with paraffin; 1% UVA-1)

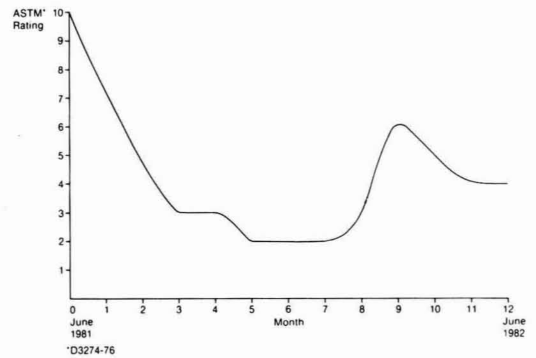


Figure 18—Relative mildewcidal activity of light stabilizer combinations (0% mildewcide with paraffin; 1% HALS 3)

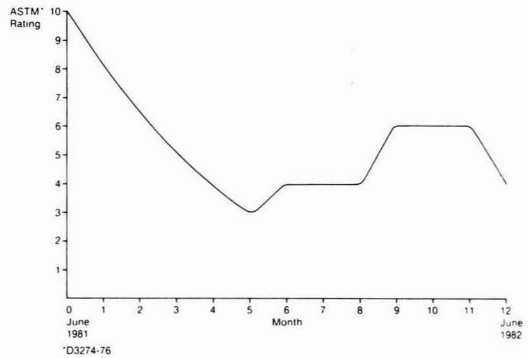


Figure 19—Relative mildewcidal activity of light stabilizer combinations (0% mildewcide with paraffin; 2% UVA-1, HALS 3)

It was necessary to establish any biocidal contribution the light stabilizers may have had. *Figures* 16–19 demonstrate the lack of mildewcide activity of the UVA and HALS 3 in combination or individually. The formulation containing no mildewcide and no stabilizer were not appreciably different from the formulations containing no mildewcide and various amounts of stabilizers. This illustrates that, in this study, the light stabilizers are not acting as mildewcides. *Figures* 20 and 21 demonstrate the performance of stabilized versus non-stabilized systems.

Figures 16 through 21 also demonstrate distinct seasonal variations of mildew defacement. This reflects the life cycle of mildew present on a surface and possibly the extremes and variability of season and geography. It is a good example of why the film model was necessary.

A statistical analysis of variance was performed on the six-month mean mildew ratings. All levels of the unstabilized mildewcide monthly ratings were compared to their respective stabilized levels to determine significant differences between stabilized and unstabilized mildewcides. A total of 136 samples were represented in this study. The result of this analysis indicated that stabilized mildewcides performed significantly better than unstabilized mildewcides (*Figures* 22 and 23).

This statistical analysis compared the mean mildew rating of stabilized and unstabilized fungicide from 132 samples ranging in fungicide concentration from 0.25% (w/w) to 2.5% (w/w) using the Repeated Measures Analysis of Variance process. Duncan's Multiple Comparison Procedures were used to determine occurrence of specific differences.[14,15]

Figures 24A through 24I are photographs which illustrate the effects of one-year outdoor exposure. Shown are a blank control containing no biocide (*Figure* 24A), 0.5% Mildewcide (*Figure* 24B) and 0.5% Mildewcide 1 stabilized with UVA 1, and a combination of UVA 1 and HALS 3 (*Figures* 24C, 24D, 24E). Panels containing Mildewcide 2, alone and in combination with light stabilizers and combinations are also shown. (*Figures* 24F through 24I).

It is clear that examination of all levels of mildewcides showed benefit from light stabilization.

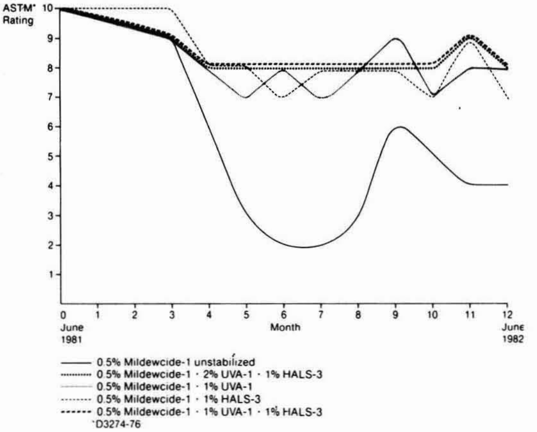


Figure 20—Relative mildewcidal activity (0.5% Mildewcide 1)

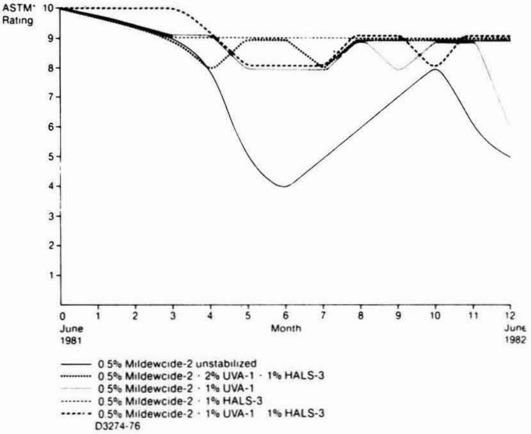


Figure 21—Relative mildewcidal activity (0.5% Mildewcide 2)

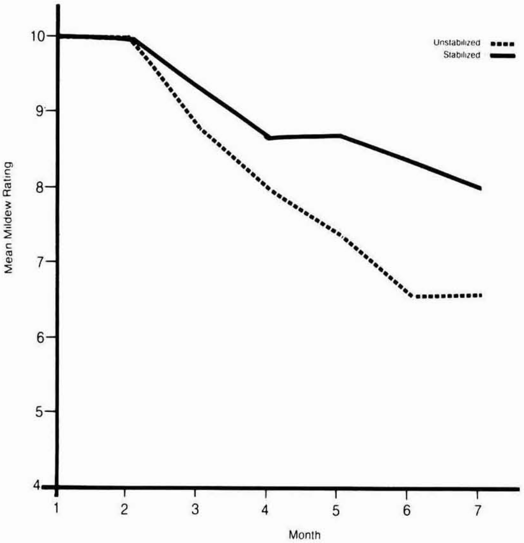


Figure 22—Analysis of variance, stabilized vs unstabilized mildewcides (Formulation: *trans*-1,2-bis(n-propylsulfonyl)-ethene)

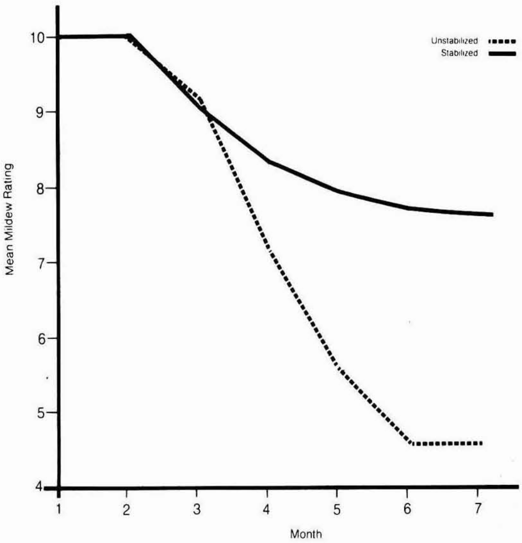


Figure 23—Analysis of variance, stabilized vs unstabilized mildewcides (Formulation: 3-ido-2-propynl butyl carbamate)

DISCUSSION

Experimental results demonstrate that light stabilizers can extend the useful service life of biocides in coatings. Laboratory model systems demonstrated the UV degradation of biocides and the presentation of biocide properties by the additive of UV stabilizers. However, no stabilizer performance evaluation should be entirely based on artificial light source exposure results.

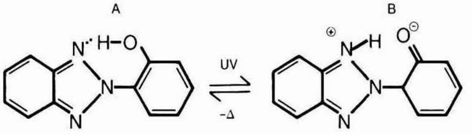
The real proof of stabilizer benefit was, however, best illustrated in the exterior exposure results. Results demonstrated the direct protection of the biocide as in the stain containing 3-Iodo-2-propynlbutyl carbamate, and indirect protection as in the stain containing 1,2-bis(propylsulfone)ethene. The concept of stabilization was clearly reinforced by the statistical analysis of variance comparing the mean mildew ratings of the stabilized vs unstabilized stains.

The reasons for this are directly related to the unnatural intensity and wavelengths of light emitted from artificial light sources. Artificial sources which exhibit any emission below 290 nm produce wavelengths of light not found in terrestrial sunlight. Wavelengths less than 290 nm, even when at low intensities, produce photochemical changes not naturally possible under direct sunlight conditions. This was clearly controlled in our model systems by the choice of borosilicate glass, which effectively screens light below 290 nm.

Another important factor in artificial weathering systems is the apparent relationship between the quantity of light striking a light stabilizer and its performance response. This implies that the intensity of light can affect the efficiency and effectiveness of stabilizer performance.

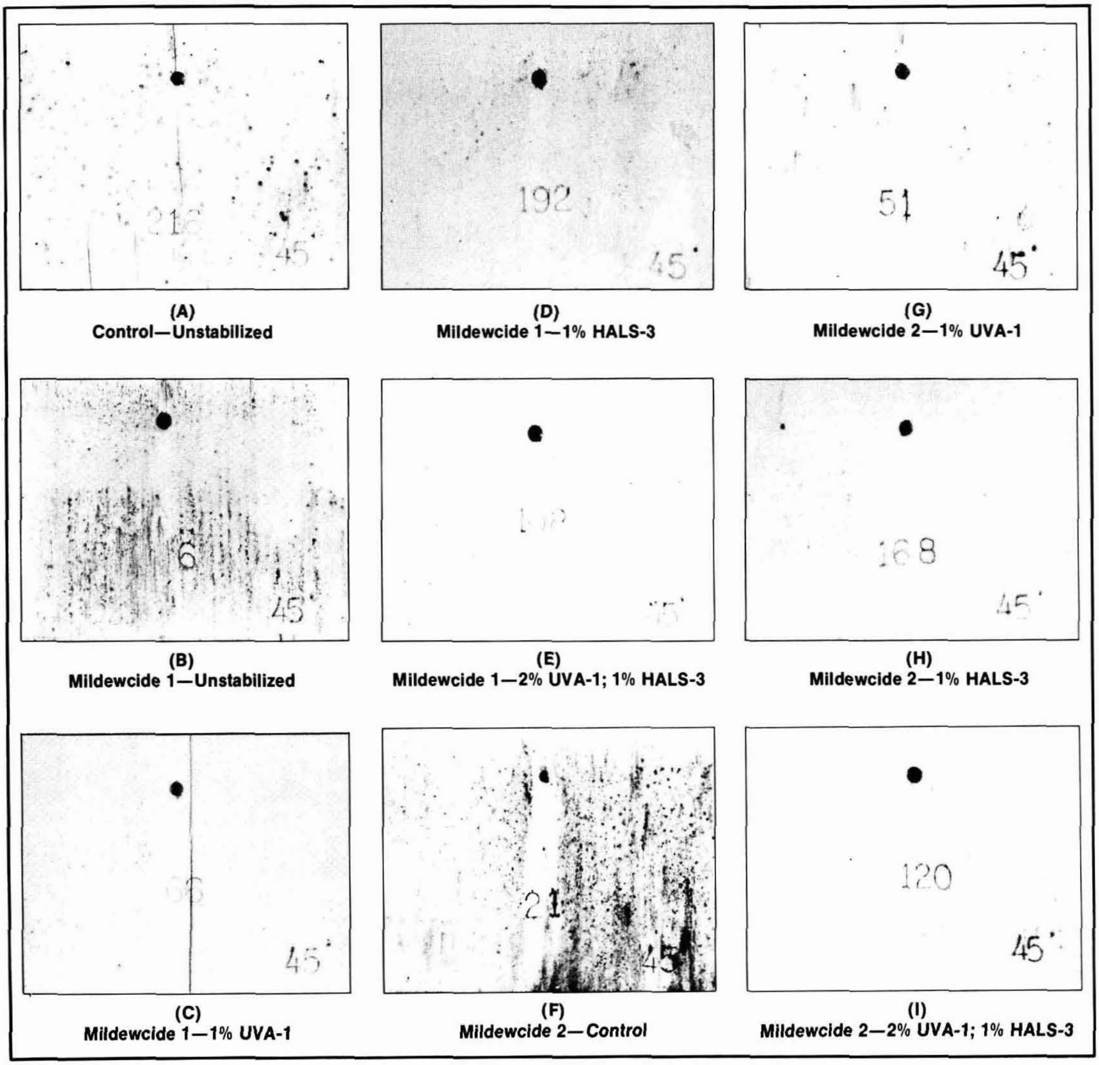
Stabilizers vary in their mechanism of protection. Stabilizer mechanisms are designed to interfere with Steps 1–4 (see equation (1)) in the photo-oxidation scheme (see Introduction); in UV absorption (Step 1); excited state energy transfer (Step 2); radical termination (Step 3); antioxidation (Step 4); or peroxide decomposition. As the term implies, ultraviolet light absorbers function primarily by absorption of UV light. The efficiency of this class of protection is critically dependent upon film thickness. The thicker the film the greater the efficiency of a UVA at a fixed level. Conversely, the thinner the film the higher the concentration of UVA is required. The critical limitation of a UVA, however, is at the air-surface interface where film thickness is zero; here even high concentrations of UVA are of limited use. It is, therefore, at this interface where photo-oxidation is likely to begin.

This study has demonstrated the use of an ultraviolet absorber (UVA 1) and a radical terminator (HALS 1, 2, 3). The mechanism of action of the benzotriazole type ultraviolet absorber is hypothesized to absorb UV radiant energy and dissipate it harmlessly as heat.[16] This conversion of radiant energy to heat is believed to happen through a tautomeric shift as follows:



(2)

In contrast, the hindered amine light stabilizers do not act by absorbing UV. In fact, the HALS are transparent to ultraviolet radiation at wavelengths longer than 200



(A)
Control—Unstabilized

(B)
Mildewcide 1—Unstabilized

(C)
Mildewcide 1—1% UVA-1

(D)
Mildewcide 1—1% HALS-3

(E)
Mildewcide 1—2% UVA-1; 1% HALS-3

(F)
Mildewcide 2—Control

(G)
Mildewcide 2—1% UVA-1

(H)
Mildewcide 2—1% HALS-3

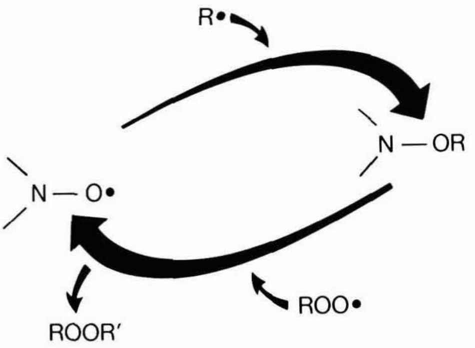
(I)
Mildewcide 2—2% UVA-1; 1% HALS-3

Figure 24—Stabilized and unstabilized panels coated with linseed oil-based stain following one year of exposure, 45° South, New York

nm. Hindered amines appear to react with free radicals to form less harmful by-products. This class of light stabilizer, therefore, is thought to interfere in Step 3 (see equation (*1*)), preventing the formation of radicals.

The precise mechanism of HALS action is not fully understood; however, many mechanisms have been proposed.[10,11] One theory which helps explain the HALS efficiency is the formulation of a stable nitroxyl radical which in turn combines with the free radical formed in the different stages of auto-oxidation and photo-oxidation. The stabilization mechanism is also presumed to be catalytic in nature, thus, deactivating free radicals in a cyclical process, ending in the regeneration of the initial nitroxyl radical. The scheme (equation (3)) describes this process:

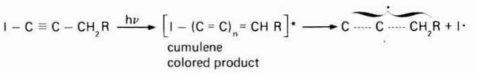
HINDERED AMINE MECHANISM OF RADICAL TERMINATION



(3)

Stabilization can be system specific for intrinsic as well as extrinsic reasons. Again, HALS provided protection in most of the artificially weathered film models, whereas, UVA's were successful in all cases. Here again it must be emphasized that the film model was principally designed to screen and identify biocide photo-oxidation. While performance of light stabilizers is academically interesting, formulators are encouraged to test responses in their own systems.

From the UV spectra of 3-iodo-2-propynl butyl carbamate, a small but apparently significant absorption occurs at the shorter wavelengths of terrestrial UV. However, more importantly, halogens like the iodo group are good leaving groups in photosensitive organic materials. Therefore, it is likely the degradation process begins with the photolysis of the iodo group from the acetylene functional end. A possible and likely photochemical change resulting in color change can be attributed to the formation of a cumulene as follows:

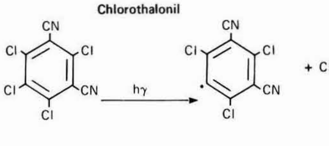


$$\mathrm{I-C\equiv C-CH_2R} \xrightarrow{h\nu} \underset{\text{cumulene colored product}}{[\mathrm{I-(C=C)_n=CH\,R}]^{\bullet}} \longrightarrow \overbrace{\mathrm{C \cdots C \cdots CH_2R}}^{\bullet} + \mathrm{I}^{\bullet}$$

(4)[16]

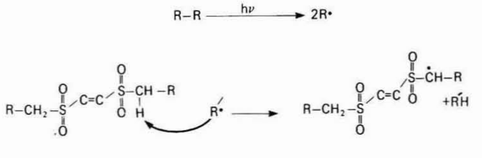
The exterior performance of stabilized vs unstabilized trans-1,2-bis(propylsulfonyl)ethene raises an interesting point of discussion: Why is stabilization a benefit to this biocide since the intrinsic architecture of the molecule does not predispose it to photochemical activity?

The answer is most likely that the protection to this biocide is probably indirect: through the protection of the biocides' surrounding environment. Such protection is likely to reduce the potential radical attack of the molecule through interruption of the photodegradation of photosensitive elements in proximity to trans-1,2-bis(propylsulfonyl)ethene in the film. We interprete the failure of (1) the unstabilized trans-1,2-bis(n-propylsulfonyl) ethene formulation and (2) the formulas containing only stabilizers (UVA; HALS, UVA & HALS) without trans-1,2-bis(propylsulfonyl)ethene in contrast to the excellent performance of the stabilized trans-1,2-bis (propylsulfonyl)-ethene as supporting the hypothesis of indirect protection. This is additionally supported by the fact that trans-1,2-bis(propylsulfonyl)-ethene did not decompose in the acrylic film model in exposures in excess of 500 hours or up to one month outdoor exposure. Under these conditions, the mechanisms of degradation may possibly occur as follows:



(5)[16]

Contrasting the indirect scheme of degradation and stabilization is the direct protection of molecules like pentachlorophenol and chlorothalonil. These are aromatic halogenated biocides with known histories of ultraviolet light instability. Upon irradiation, it is likely that the loss of a chlorine atom initiates the decomposition scheme:



(6)

The results indicate that both a UVA and a HALS individually were capable of protecting exterior exposed biocides. It must be recognized that these results refer specifically to the mildew rating and not to the combination of other properties of weathering such as chalking, erosion, and general aesthetic appearance. It is commonly observed that combinations of UVA's/HALS act synergistically to protect materials from photo-oxidation. It was our impression that the most consistent performance and overall best general appearance of surface was apparent in formulations stabilized with the combination of UVA and HALS.

Biocide stabilization is a unique approach with significant benefits. The major advantage is in the extension of service life, as for example the four-fold increase in performance level of 3-iodo-2-propynl butyl carbamate and trans-1,2-bis(propylsulfonyl)ethene. Consequently, incorporation of UV stabilizers into a coating can extend the useful service of the coating itself, protecting not only the biocide, but, in addition, the binder as well as any other photosensitive components. The end result is a more durable, functional, and serviceable protective coating.

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THIS PAPER WAS AWARDED FOURTH PRIZE IN THE 1982 ROON AWARDS COMPETITION

Presence and Effects Of Anaerobic Bacteria In Water-Based Paint. I

Robert A. Oppermann and Milton Goll
Cosan Chemical Corporation*

Water-based paints are subject to microbial invasion resulting in spoilage. Analysis of such spoiled paints frequently results in no known chemical or biological cause being found. Bacteria growing in the absence of oxygen (anaerobically) could cause some of the deterioration, but would not be found in the aerobic culture methods normally used. Accordingly, many paint and paint raw material samples, some of which were spoiled, were cultured under anaerobic conditions. Anaerobic bacteria which reduce viscosity and cause malodors and discoloration were found. The quantity, identification, degradation activity, biocide sensitivity, and prevention of the bacteria found are discussed.

INTRODUCTION

The history of microbial deterioration of paint began with the use of paint itself. While paints were nonaqueous, the primary problem was growth of fungi on the paint film (mildew). With the introduction and ascendency of waterborne coatings, a second form of microbial attack was born. Bacterial contamination of the fluid paint could cause spoilage in the form of loss of viscosity, gassing, pH shifts, off odors, and even gellation.

Even though the use of microbiocides substantially reduced contamination of paints, there are still unexplained problems. For example, occasionally no microorganisms are found in a paint that was gassing or had shown a viscosity loss. After elimination of possible chemical causes, the usual explanation for this condition is that microbes were present but died, or they were killed by the use of a slow acting microbiocide. A second explanation, in the case of loss of viscosity, is that an enzyme (a biocatalyst) came into the system with a raw material and there was no bacterial contamination of the paint. The enzyme, in this case, was the causative agent of the viscosity loss.

There is a third possible explanation for these occurrences—microbes exist in the paint, but were not found in the normal process of microbiological examination. Such microbes may have exacting nutritional requirements or they may be anaerobic, that is, they may not require the presence of air and, in fact, they are inhibited or killed by atmospheric oxygen. The concept of specific nutritive requirements for contaminating microbes has been examined and nothing new has been found. This leaves the possible presence of anaerobic bacteria in the paint. This possibility had indirectly been examined during the early investigations of paint degradation when lists of bacteria and fungi found in paint were reported.[1,2] Even though there has been no direct study for the presence of anaerobes in a water-based paint, a few papers have obliquely noted the existence of anaerobes. A British paper[3] noted the presence of the "sulfate reducers," and unidentified gram positive and gram negative "sporeformers," were mentioned in an American paper.[4]

Early spoilage research naturally followed the more easily grown aerobes, the bacteria requiring oxygen. The identification of anaerobic growth has been difficult because of the materials and methods which were available. Reducing agents were added to the growth medium to be used, and rather cumbersome and inadequate anaerobic conditions were obtained by the use of illuminating gas and platinum catalysts. All of this led to a certain reluctance to look for anaerobes. Also of concern was the possibility that the reducing agent(s) used in the medium were adversely affecting the growth of the anaerobes and not all organisms that would grow under anaerobic conditions would be found using this type of medium.

In the last few years, new methods of growing anaerobic bacteria have been developed. This is primarily due to the interest of the medical community in anaerobic infections and the fermentation industry in the possibility of using anaerobes for new fermentation products. While improved anaerobic jars are still used to a great extent, there has been the development of complete anaerobic

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*400 14th St., Carlstadt, NJ 07072.

cabinets in which all the normal microbiological processes can be accomplished under completely anaerobic conditions. These cabinets have made the isolation, identification, and determination of the bio-chemical characteristics for anaerobes much easier than it has been previously. Therefore, the time was appropriate for a new microbiological survey of water-based paints, specifically seeking the presence of anaerobic bacteria, with the hope of solving the problem of undetermined biodeterioration. An examination of paint and paint raw materials for the presence of anaerobic bacteria has been undertaken. Many anaerobic organisms have been found and some of their growth characteristics determined.

MATERIALS AND METHODS

The initial detection and isolation of microbes was carried out using an anaerobic glove cabinet.* This cabinet maintains strict anaerobic conditions, so even fastidious anaerobic organisms can be cultivated, isolated, and identified.

The unit is primarily a glove box containing a constant atmosphere of 85% nitrogen, 10% hydrogen, and 5% carbon dioxide. Stringent anaerobic conditions are maintained within the cabinet by means of a cold palladium catalyst which combines any oxygen which enters with hydrogen to form water. The water is removed by a desiccant. Both desiccant and catalyst can be regenergated in a laboratory oven.

Initial culturing was made by streaking the sample into a divided Petri Dish containing, in one half, Brain-Heart Infusion Agar (BHI)†, and in the other half a nutrient for the growth and detection of the sulfate reducing bacteria, (Medium E of Postgate, without thioglycolate).[5] The Petri Dishes were incubated for up to two weeks at 30°C in the anaerobic incubator which was an integral part of the cabinet. Observations of the streaked samples on the agars were made at 1, 3, 5, 7, and 14 days. If isolated colonies were obtained on initial streaking, they were transferred to Typtic Soy Agar (TSA)† slants for storage and later identification. Where confluent growth was obtained from massive contamination, the growth was restreaked on BHI Agar plates and the now isolated colonies were transferred to slants. In all cases, the isolates were also streaked onto a BHI plate to determine if growth would occur in air, thus indicating the presence of facultative anaerobes.

Identification procedures for the anaerobes made use of the API-20A System** containing 21 different tests. Confirming tests were carried out in 20 mL screw cap tubes containing standard medium for nitrate reduction, hydrogen sulfide production, and growth in 20% bile.[6]

Facultative anaerobic bacteria were identified using the Fisher Entero Set 20 System.†† All of these bacteria were gram negative rods, many from the family Enterobacteriaceae, which inhabit soil and the intestinal tract. Supplemental tests were performed, where needed, using screw cap tubes for nitrate reduction, pigment production, gelatin digestion, and motility.[6]

The basic medium for the identification of the utilization of paint components was a modified Bushnell-Haas medium,[7] a mineral salts medium, using only one-half the original concentration of phosphate, 1% of the paint ingredient, plus 0.02% yeast extract. Essentially, the only source of carbon for growth and energy was the organic paint component. There was practically no growth and no change in the pH indicator with any of the cultures in this medium without the paint ingredient.

To determine if any of the isolated anaerobic bacteria could cause viscosity losses, the organisms were added to tubes of a sterile medium containing hydroxyethyl cellulose (HEC). The HEC medium used consisted of hydroxyethyl cellulose 1.5%, NH_4HO_3 1.5%, Na_2HPO_4 0.5%, KH_2PO_4 0.5%, MgSO $5H_2O$ 0.1%, CaCl 0.05%, $FeSO_4$ 0.01%, Yeast Extract 0.05%, and Polypeptone 0.1%,*** adjusted to pH 7.5 with NaOH.

The loss of viscosity of the medium was determined by simple up ending of the tubes of medium and comparing with an uninoculated tube. The time in days required to reach a water-like consistency was recorded.

The Minimum Inhibitory Concentration (MIC) tests of the facultative anaerobes were carried out using Nutrient Broth*** plus 0.05% ascorbic acid. Either Nutrient Broth of Brain-Heart Infusion Broth† plus 0.05% ascorbic acid was used for anaerobic bacteria. The small amount of ascorbic acid acts as an oxygen scavenger under anaerobic conditions, but does not greatly affect the medium under aerobic conditions.

RESULTS

One thousand samples which Cosan had received for normal microbiological assay were examined under anaerobic conditions. The number and nature of the samples are presented in *Table* 1. The two largest classes of samples were latices and slurries. Wash water and paints each number approximately 70, but only seven thickeners were sampled.

The results of the anaerobic culturing of these materials are shown in *Table* 2. From this table, it can be seen that 5.8% of all the samples examined contained anaerobic bacteria. The true anaerobes were most often found with bacteria which were facultative anaerobic, that is, able to grow with or without the presence of atmospheric oxygen. One could lump the anaerobes with the facultative anaerobes and sulfate reducing bacteria and say that anaerobic growth was 11.7%.

The anaerobes were often found in the presence of other bacteria, so only the contaminated samples may be considered, and then it can be said that 27.2% of the contaminated samples contained anaerobes. This is almost one-third of the contaminated samples received. Only a small percentage of the total number of samples, 1.7%, showed the presence of anaerobic bacteria where no aerobic contamination was found. Nevertheless, this was

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*Model 1024, Forma Scientific, Marietta, OH.
†Difco Laboratories, Detroit, MI.
**Analytab Products, Plainview, NY.
††Fisher Scientific Co., Orangeburg, NY.

***BBL, Div. Becton Dickinson Co., Cockeysville, MD.

Table 1—Materials Cultured for the Presence of Anaerobes

Type	Amount
Latex emulsions	534
Slurries, TiO_2, Clay	207
Wash waters	73
Paints	72
Surfactants	51
Color pigment dispersions	43
Skins, Incrustation, etc.	13
Thickeners	7
	1000

Table 2—Anaerobes Found in Samples

Number of Samples	Sterile	Anaerobes	Facultative Anaerobes	Sulfate Reducers	Aerobic Contamination
1,000 ...	787	58 5.8%	52 5.2%	7 0.7%	196

Anaerobes in contaminated samples = 27.2%

Anaerobes where no aerobic contamination was found = 1.7%

24% of the total number of anaerobes isolated. Only seven samples, or 12% of the total anaerobes, showed the presence of sulfate reducing bacteria.

The sulfate reducing bacteria are present in small but important numbers. The sulfate reducers, in order to grow, reduce sulfate ion $SO_4^=$ to sulfides and hydrogen sulfide, which smells like rotten eggs. Therefore, although their numbers are small, the growth of these bacteria in a product or raw material usually means it must be discarded. There is no inexpensive or easy method to rid the material of the bad odor or the black "sulfide staining," which usually accompanies it.

Table 3 shows the distribution of the anaerobes found. When the number of samples of each type is considered, finished paint had the highest percentage of anaerobic contamination, 11.8%. Although latices had the highest findings of anaerobes, the larger number of samples reduced the percentage to 6.4%.

The anaerobic bacteria found in these contaminated samples are identified in *Table* 4. The frequency of finding these organisms is also noted. By far the largest group of anaerobes found were members of the genus *Bacteroides* which accounts for 44% of the isolates. The genus *Clostridium* is next with 24%, and *Desulfovibrio* (the sulfate reducers) claims 12% of the total. It can easily be seen that these three genera made up 70% or about three-quarters of the bacteria found.

Many of the organisms found are listed in *Tables* 4 through 7 as "species." This is because the identification of anaerobic species is very difficult, as any of the identifying characteristics are variable within the group. Rather than listing some doubtful species, it was decided to identify them only by the genus name.

By far the largest group of contaminating anaerobes found were gram negative, non-sporeforming rods. The findings of so many non-sporeforming types is surprising because it would be expected that they would not be as persistent as the sporeforming species.

Because a large number of facultative anaerobes were found, it was decided to isolate and identify these organisms also. The facultative anaerobes found are listed in *Table* 5. It was thought that a great number of these organisms would be members of the genus *Pseudomonas*, however, there were more findings of *Serratia marcescens*, followed by the genera *Enterobacter*, *Hafnai*, and then *Pseudomonas*. Most of these organisms are also found as aerobic contaminants of paint and paint raw materials. Only two of the organisms are seldom seen as "normal" contaminants, *Hafnia alvei* and *Serratia liquefaciens*. These may have been found in these studies because of the anaerobic culturing. Under anaerobic conditions, they may be overgrown or otherwise lost and not noted.

Degradation of Paint Components

The presence of anaerobes in a paint or raw material means that the organisms must be able to live on one or more ingredients in that material. There are two soluble organic materials found in large quantities in paints or water-based materials used to make paints. There are cellulosic thickeners and one or more surfactants/dispersing agents.

When the anaerobic organisms were tested for their ability to digest a common cellulosic thickener, hydroxyethyl cellulose (HEC), it was found that approximately 38% of the isolates would cause a viscosity loss in HEC solution (See *Table* 6). It was also apparent that many of these organisms were not strongly cellulolytic, as two to three weeks or more were required to cause a major viscosity loss. The organisms involved are mainly members of the genera *Bacteroides* and *Clostridium* which constitute the majority of the bacteria isolated. All but one organism produced acid in its digestion of HEC.

When the isolates were tested for their ability to utilize a surfactant, it was found that 45.6% (26% of the isolates) would utilize surfactants which were the "salts of polymeric carboxylic acids." These results are presented in *Table* 7. It was noted that acid, and in one case gas,

Table 3—Distribution of Anaerobes

	Anaerobes	Sulfate Reducers
Paints	11.8% (8)[a]	2.7% (2)
Wash waters	9.6% (7)	6.8% (5)
Skins, Incrustations, etc.	7.7% (1)	0
Color pigment dispersions	7.0% (3)	0
Latex, Emulsions	6.4% (34)	0
Slurries, TiO_2, Clay, etc.	2.4% (5)	0
Surfactants	0	0

(a) The percentage of anaerobically contaminated samples is shown by the first number and the actual number found is shown in parenthesis.

Table 4—Anaerobes Found in Contaminated Samples

	Frequency
Actinomyces israelii	2
Bacteroides clostridiiformis	2
Bacteroides fragilis	5
Bacteroides hypermegas	1
Bacteroides ovatus	2
Bacteroides species	9
Bifidobacterium adolescentis	5
Clostridium butyricum	3
Clostridium sphenoides	2
Clostridium subterminale	1
Clostridium species	7
Desulfovibrio desulfuricans (sulfate reducer)	7
Eubacterium aerofaciens	1
Lactobacillus fermentum	3
Peptococcus saccharolyticus	1
Streptococcus intermedius	3

Table 6—Effect of Anaerobes on Hydroxyethyl Cellulose Medium

Organism	Time in Days to Water-Like Viscosity	Acid Produced[a]
Bacteroides species A	7	+
Bifidobacterium adolescentis	7	+
Clostridium species III	7	+
Clostridium sphenoides	7–10	+
Clostridium butyricum	7–21	±
Bacteroides hypermegas	14	+
Clostridium species I	14–21	+
Bacteroides ovatus	14–21	+
Bacteroides species C	21	−
Peotococcus saacharolyticus	25	±
Eubacterium aerofaciens	37	+
Unidentified short rod	39	+
Lactobacillus fermentum	40	+

(a) + = Acid produced; − = No acid produced; ± = Slight amount of acid produced.

could be produced from this material in three weeks. Other surfactant materials may also serve as substrates for the production of acid or gas.

Effects of Microbiocides

The usual response to the presence of contamination is the use of a microbiocide, either to prevent contamination or to return the product to a sterile condition.

When the representative anaerobic bacteria were tested against some of the commonly used microbiocide types, it was noticed that differences occur between anaerobic bacteria and aerobic bacteria. These results are shown in *Table* 8. In most cases, more preservative is needed to kill the anaerobes than the mix of aerobic bacteria. Of the three organisms used, the *Bifidobacterium adolescentes* required the greatest concentration of the biocide. It was less susceptible than *Clostridium butyricum* which, because of its spores, would be expected to be more resistant than the two non-sporeformers.

Microbiocides of representative types were also tested against facultative anaerobes under both aerobic and anaerobic conditions. Differences were again seen in the results (see *Table* 9). There are some obvious changes in the sensitivity to the biocides, but the differences were not consistent. The adamantane biocide in the test did not produce sterility at reasonable levels. Indeed, none of the remaining three preservatives tested showed consistent effects either between aerobic-anaerobic conditions or between the two bacteria.

Table 5—Facultative Anaerobes Found in Contaminated Samples

- *Citrobacter freundii*
- *Enterobacter aerogenes*
- *Enterobacter cloacae*
- *Escherichia coli*
- *Hafnia alvei*
- *Klebsiella species*
- *Proteus mirabilis*
- *Pseudomonas aeruginosa*
- *Serratia liquefaciens*
- *Serratia marcescens*

The reason for the differences was attributed to the dramatic shift in the metabolism of the organism in the change from aerobic to anaerobic conditions. Each microbiocide affects a particular point, or points, in the metabolism of the organism. When a different series of metabolic pathways is used, the microbiocide may not be as effective as it was earlier unless the biocide affects a critical point in all biochemical pathways. The excellent performance of phenyl mercury microbiocides indicates that critical enzymes, probably containing the sulfhydryl group (R-SH) or the disulfide linkage (R-SS-R),[8] are important in the metabolism of anaerobic bacteria as well as aerobic bacteria.

DISCUSSION

The findings of anaerobes in paint, paint raw materials, and paint wash waters is of great significance to the Paint Industry. From the data in *Table* 6, it appears that many of the anaerobes found in paint could be a cause of viscosity loss in paints. The time required for this viscosity loss varied with the organism involved. In some cases, the time required to drop to water-like consistency was one week, and in other cases, much longer.

The degradation activities of aerobic organisms are greater, faster, and more efficient than that of anaerobes.[9] The process of oxidation by use of atmospheric oxygen allows almost all organic molecules to be attacked by aerobic microbes. Under anaerobic conditions, most attack is of a hydrolytic or simultaneous oxidation-reduction type which most often leaves large acidic fragments in the medium and less energy is obtained.

These acids could react in a paint with any calcium carbonate which was present as a filler or secondary pigment and produce carbon dioxide gas. This slow production of acids and, therefore, evolution of carbon dioxide, would explain the slow production of gas which sometimes occurs after canning.

Nutrients for Bacterial Growth

The growth of anaerobes in surface-active "salts of polymeric carboxylic acids," indicates that this type of material may be among the possible nutrients for anaerobic bacteria. A second group of possible nutrients for the anaerobes are the by-products from aerobic contaminants which are often found with the anaerobes in a contaminated paint.

Aerobic contamination of paint can fulfill two requirements of the anaerobic contaminants, the first being the exhaustion of oxygen from the immediate environment by aerobic metabolism and, the second being the possible production of nutrients for anaerobes.

In consideration of the above, it is interesting to note the number of facultative anaerobic bacteria that appeared in this examination. These organisms, because of their ability to metabolize products either aerobically or anaerobically, are in an ideal position. After the paint can has been closed, these organisms can take part in the initial exhaustion of oxygen and degradation of the paint and, when anaerobic conditions are accomplished, convert to an anaerobic metabolism and continue their activities.

Sulfate Reduction

The most distinctive anaerobic growth that can occur in wash waters and paints is the growth of the sulfate reducers. The amount of hydrogen sulfide produced can be so great (10 grams per liter)[9] as to render wash waters uesless for future paint production. It is the odor of the H_2S and its chemical activity on pigments and on corrosion that causes this material to be useless. Sulfate reduction would entail the disposal of the contaminated wash water, an additional expense to the manufacturer.

The metabolism of the sulfate reducers in paint is an interesting problem. Normally, these organisms will use hydrogen obtained in oxidizing a donor compound. These are usually simple organic acids such as lactic, succinic, or malic acids—types which are not used in paint. The following summary equation for the reduction of sulfate ion shows a large amount of hydrogen is required to obtain the energy necessary for life:

$$SO_4^{=} + 10H^+ + 8e^- \longrightarrow 4H_2O + H_2S + \text{Energy} \qquad (1)$$

The question then becomes, "Where do the sulfate reducers obtain the hydrogen donors necessary for their growth?" One suggestion, made above, is that many of the by-products produced by aerobic contamination would be suitable for use by anaerobes and, in this case, the sulfate reducers. By-products known to occur in normal aerobic metabolism are lactic, acetic, malic, and succinic acids. Most of these materials are excellent hydrogen donors for sulfate reduction. Perhaps the problem with the sulfate reducers occurs primarily because of aerobic contamination which has produced the hydrogen donor(s) later needed for sulfate reduction.

Table 7—Effect of Anaerobes on Salts Of Polymeric Carboxylic Acid Surfactants After Three Weeks Incubation

Organism	Growth[a]	Acid	Gas
Bacteroides fragilis	+	−	−
Bacteroides hypermegas	++	±	−
Bacteroides ovatus	+	±	−
Bacteroides species C	+	−	−
Bacteroides species I	++	++	−
Clostridium butyricum	++	±	−
Clostridium sphenoides	+	−	−
Clostridium subterminale	+	±	+
Clostridium species A	+	+	−

(a) ± = Slight production; + = Slight-moderate growth; ++ = Moderate to heavy growth; +++ = Very heavy growth; − = No growth.

"Ecology of Paint"

In essence, the problem of microbial growth in a paint product is one of ecology. Obviously, there are certain organisms (for example, *Pseudomonas sp.*) capable of degrading a great many organic compounds. Such organic compounds may occur in paint. The *Pseudomonas sp.*, or other aerobic contaminants, in their normal metabolism, produce by-products which are capable of being utilized by other organisms which may be present. The other organisms in a symbiotic relationship now are able to furnish the *Pseudomonas sp.* with additional nutrients from their metabolism which allow an expansion of the activities of *Pseudomonas.* Together, such associates of organisms are capable of destroying many products that either alone would be incapable of utilizing. When mixed cultures of bacteria are at work within a paint, various by-products can be produced which will then serve as

Table 8—Effect of Preservatives on Anaerobic Bacteria Minimum Inhibitory Concentration in Parts per Million

Preservative Type	Laboratory[1,2] Mixture	*Bacteroides fragilis*	*Bifidobacterium adolescentis*	*Clostridium butyricum*
Isothiozoline type	300	100–150	>500	150–200
Triaza adamantane chloride type	>1000	>1000	>2000	>2000
Oxazolidine type	>1000	800–900	>2000	1600–2000
Phenyl mercuric type	8[a]	5–6	50	20–30

MIC on Laboratory Mixture Performed In Air. Mix contains approximately equal numbers of *Pseudomonas aeruginosa*, *Enterobacter aerogenes*, *Escherichia coli* and *Proteus mirabilis*.
(a) PPM as mercury metal

Table 9—Effect of Preservatives on Facultative Anaerobes Minimum Inhibitory Concentration in Parts per Million

	Enterobacter cloacae		*Hafnia alvei*	
Preservative Type	**Aerobic**	**Anaerobic**	**Aerobic**	**Anaerobic**
Isothiazoline type	25-50	150-200	50-75	50-75
Triaza adamantane chloride type	>1000	>1000	>1000	>1000
Oxazolidine type	900-1000	>1000	>1000	>1000
Phenyl mercuric type	1.2-2[a]	6-7	6-7	6-7

(a) PPM as mercury metal.

nutrients for anaerobic organisms, such as sulfate reducers, which may also be present but not actively growing because of the presence of oxygen.

Today, many paint plants are reusing their wash waters. These diluted paints are placed in holding tanks until they can be used. During this time, unless a fairly high level of microbiocide has been added, aerobic contaminants naturally present are both degrading the dilute product and creating anaerobic conditions. This then allows any anaerobes to grow, perhaps in large numbers. At the time of use of these wash waters in a product, a level of microbiocide is added, but this may not be sufficient to prevent the continued growth of the anaerobes which have already grown in the stored wash water. In time, one could expect these paints to incur viscosity losses, shifts in pH, odor production, and, perhaps, gassing. It is interesting to note that more examples of gassing and viscosity loss without a definite explanation have been seen in the last two years, at the same time that more wash waters were being reused.

Use of Inhibitors

The findings of different activity of microbiocides, aerobically and anaerobically, are important because: (1) it indicates that anaerobes may not be killed by the dosage used to kill the aerobes; and (2) in situations where anaerobes thrive, they may not be damaged at all by the later addition of normal amounts of microbiocide. However, if a functional microbiocide is used initially, aerobic contamination is eliminated and the presence of oxygen will act as an inhibitor to anaerobic degradation even if the biocide's effect may be reduced for anaerobic bacteria.

Oxygen, for some of the anaerobes, is not only inhibiting but lethal! If a sensitive population is exposed to oxygen for five to 10 minutes, massive or total death of the culture results. This is usually assumed to be due to the accumulation of hydrogen peroxide. Many anaerobic bacteria lack the enzyme catalase, and so, are incapable of decomposing the hydrogen peroxide normally produced.[9] In other cases, the organisms contain vital enzymes which must remain in a reduced condition. Atmospheric oxygen oxidizes the enzymes and destroys their effectiveness.

Effects of Aerobic or Anaerobic Contamination

Anaerobic organisms produce a different series of compounds than aerobes and, to a certain extent, different effects. In the end, however, as far as the paint manufacturer is concerned, the results are similar to that of aerobic contamination, which is to say, loss of viscosity, production of off odors, color changes, and/or gassing.

With normal aerobic culturing for contaminants, the anaerobic organisms would be missed and other explanations for the cause of the deterioration of the paint where no microbes are found would be postulated. Now that it is known that anaerobic organisms can exist in paint, testing for anaerobes should always be made before evoking other explanations, such as, the organisms dying off after the paint has been canned, or enzymes coming into the system from raw materials.

SUMMARY

In conclusion, it can be said that any contamination, aerobic or anaerobic, may lead to the deterioration of a paint. In the past, the only form of contamination which was considered has been aerobic. Now, with the findings of anaerobic microorganisms in paint, a new series of tests must be utilized in order to adequately explain deterioration of some paint.

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PRI Paint Research Institute
of the Federation of Societies for Coatings Technology

PROCEEDINGS/NUMBER 154

Mildewcide Testing And Ultrastructural Analysis With *Aureobasidium pullulans*

Richard E. Crang and Susan G. Robinson
University of Illinois[*]

PRI Executive Director's Preface

The Paint Research Institute has been active in the search for fundamental knowledge bearing on the problem on the defacement of painted surfaces by mildew. The use of mercury compounds, the most effective chemicals for use in paints, and the use of other heavy metals is being discouraged.

Eight organizations collectively formed the Mildew Consortium of the Paint Research Institute. These organizations contributed regularly to the support of research with money, advice, and experimental work in their own laboratories. [Please see "The Accomplishments of the Mildew Consortium" in the December 1983 JCT.]

This report covers one of several research programs. Its objective was to obtain detailed understanding of the action of mildewcides on *Aureobasidium pullulans*, the principal organism responsible for defacement.

The work of the Mildew Consortium has also involved the preparation and tests of polymers containing mildewcides as part of their structure; efforts to understand the formation by the mildew organism of black pigment, melanin, responsible for the discoloration; the mode of release of mildewcidal ingredients from a paint film; and accelerated laboratory testing for mildewcidal activity.

Dr. Seymore Hochberg,
PRI Executive Director

Five commercial non-metal-containing mildewcides were assessed for their inhibitory levels in defined liquid cultures of *Auerobasidium pullulans*. The results of culturing, light microscopy, and scanning and transmission electron microscopy showed one mildewcide to be the most effective at sublethal concentrations in the inhibition of growth and pigment production. At low concentrations, four of the agents promoted melanization to varying degrees, although growth was still decreased. At subinhibitory levels each agent induced some amount of ultrastructural damage as seen using transmission electron microscopy. Although all were effective at high concentrations in inhibiting growth of *A. pullulans*, certain agents allowed for the growth of bacteria in laboratory stocks.

INTRODUCTION

Using liquid culture growth techniques and a combination of microscopic methods, we studied the inhibitory responses of five commercial non-heavy metal mildewcides on the common paint-defacing black mildew *Aureobasidium pullulans*. Our repeated testing has shown that although significant inhibition of mildew growth can be demonstrated with all of the compounds in defined liquid culture media, there is definite variation in the cellular responses at low dose-levels which may more closely approximate the activities of the mildewcides in coatings applications. While this report is confined to studies of growth responses of *A. pullulans* in defined

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[*] Dept. of Plant Biology and Center for Electron Microscopy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Presented by Dr. Crang at the 60th Annual Meeting of the Federation of Societies for Coatings Technology, November 4, 1982, in Washington, D.C.

Table 1—Letter Designation, Structural Formulae and Generic Description of the Five Mildew Inhibitors Employed in this Study. Letter Designations Are Entirely Arbitrary

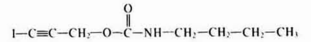
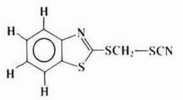
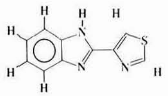
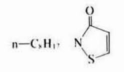
A	 $I{-}C{\equiv}C{-}CH_2{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}NH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$	3-Iodo-2-propynyl butyl carbamate
B		2-(Thiocyanomethylthio) benzothiazole
C		Sodium pentachlorophenol
D		2-(4-Thiazolyl)benzimidazole
E		2-n-Octyl-3(2H)-isothiazolone

Table 2—Composition and Preparation of Leather's Spore Medium (LSM) Used Throughout this Study. For Solid Agar Plates, 2% Difco Agar Was Added; for Liquid Cultures 0.1% Agar Was Added to Encourage Growth

***Aureobasidium pullulans* Spore Medium**

Flask A	Glucose	2.5 g
	$MgSO_4 \cdot 7H_2O$	0.25 g
	H_2O	200 mL
Flask B	KH_2PO_4	0.25 g
	$K_2H\ PO_4$	0.25 g
	$NaNO_3$	0.072 g
	H_2O	300 mL
	Agar (for solid media)	10 g

Autoclave separately. Mix at 45°C and pour into petri plates, or prepare slants.

liquid culture media, experiments are near completion of these and other inhibitory compounds in actual paint films using an artificial weathering technique previously described.[1]

METHODOLOGY

The specific inhibitors examined are designated by their generic names in *Table* 1. For the purposes of this report, trade names are not used and the inhibitors are designated by the letters arbitrarily ascribed in *Table* 1. The culture medium employed in this study is "Leathers' Spore Medium" (LSM), a formulation proposed by A. Z. Leathers, of PPG Industries, Pittsburgh, PA. Its composition is given in *Table* 2.

Cultures were transferred by washing 24 hour growth on LSM agar plates with 5 mL of sterile-distilled water. The washed spores were then either transferred directly to media plates or collected and dispensed as inoculum in 1 mL volumes to flasks containing liquid LSM. Inhibitors were either added at the time of inoculation, or, after the culture had grown for 24 hours at 28°C in total darkness in a shaking water bath. Dose levels of the inhibitors used were expressed in molar concentrations and ranged from 1×10^{-6} *M* to 1×10^{-2} *M* in the LSM medium. For 1×10^{-3} *M* solutions the following weight percent of the active ingredient was used for each inhibitor: A = 0.021 B = 0.03; C = 0.027; D = 0.021; E = 0.022. It should be noted that these concentrations are significantly less than the 0.5–1.5 weight percents recommended by manufacturers for incorporation into solvent or water-thinned paints. The concentrations used were determined by the limits of solubility in the aqueous growth medium and our intent to work at sublethal dose levels. Samples were then harvested at 48 to 96 hour total culture growth time and prepared as whole wet mounts for light microscopy. Specimens prepared for transmission electron microscopy were fixed in a buffered 3% glutaraldehyde, post-fixed in buffered 2% osmium tetroxide, dehydrated in a graded ethanol and propylene oxide series, and embedded in an Epon® 812 epoxy mixture. Ultrathin sections (700–800 Å) were cut with the aid of a Reichert OmU-2 ultramicrotome and a diamond knife. For scanning electron microscopy, glutaraldehyde-fixed specimens were dehydrated in an ethanol series, dried by the critical point method using carbon dioxide as the transition fluid, and coated with a 150 Å layer of gold-palladium prior to observation. Details of the preparations were essentially the same as those previously described.[2] Transmission electron microscopy was performed with a JEOL 100-C operating at 80 kV, and scanning electron microscopy employed the use of an ISI DS-130 instrument operating at 15 kV.

RESULTS

At 1×10^{-2} *M*, all agents tested showed complete inhibition of growth and black pigmentation (melanization) at 24 and 48 hours. *Figure* 1 shows representative samples of cultures obtained at 48 hour post-inhibition at inhibitory agent concentrations of 1×10^{-3} to 1×10^{-6} *M*. At the lowest concentration (1×10^{-6} *M*), all inhibitors showed as much growth density (turbidity) as controls (no inhibitory agents), and most were as melanized or

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Epon is a registered tradename of Shell Chemical Co.

more so than the control cultures. This turbidity is rated as ++++ (the highest level observed at this time period). Other turbidities are rated on a relative basis but determined from washed cell masses. Only inhibitor A was completely effective in preventing melanization at a concentration of 1×10^{-5} *M*, although slight turbidity (+) could be observed. Inhibitors B and C showed the greatest turbitidy (++++) and melanization. At the highest inhibitory concentration shown in *Figure* 1 (1×10^{-4} *M*), A, B, and E were effective in preventing melanization, and B and E showed the lowest turbidity (+). Agents C and D showed little inhibition of melanization but did retard turbidity (++). In plate cultures at the same inhibitor concentrations, melanization and growth inhibition were much the same as in liquid media after 48 hour post-inoculation, but all plates showed some degree of melanization after the course of two weeks. Again, agent A was most effective in delaying the onset of melanization. Similar results were obtained at 72 hour post-inhibition in liquid media (*Figure* 2) where, at 1×10^{-4} *M* concentration, all agents showed heavy melanization equivalent to control cultures except for A. At this extended time, even inhibitor A showed moderate turbidity (++) and the onset of melanization. Thus, time as well as concentration, played a significant role in the melanization process, and the process occurred at a much accelerated rate in liquid media over that on agar plates. It is possible that over the course of time *A. pullulans* could adapt to the presence of the mildewcides and that the mildewcides may degrade.

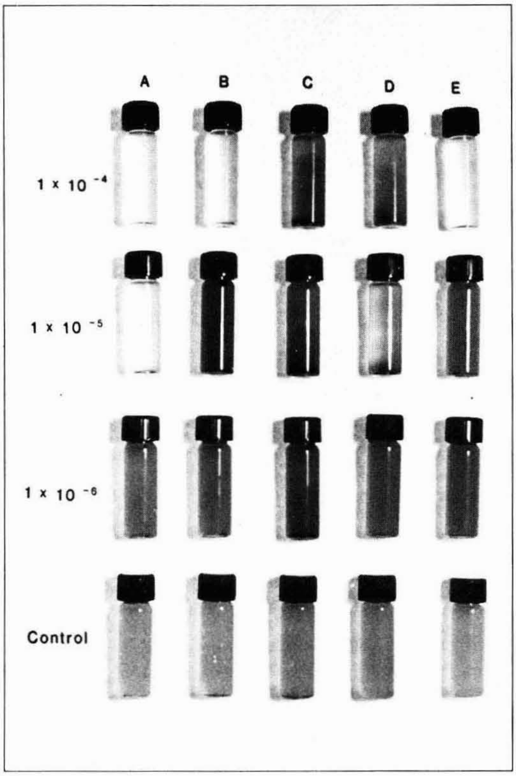

Figure 1—Aliquots of specimen cultures showing turbidity and melanization effects of the five inhibitory agents at three molar concentrations. All control cultures lacked mildewcides. Results are shown from 48 hr post-inhibition (72 hr total growth). At the lowest inhibitory concentration (1×10^{-6} *M*), pigmentation of *A. pullulans* was often found to be darker than that of controls

Samples of the cultures were taken for microscopic observations at 48 hour post-inhibition intervals from flasks containing 1×10^{-4} *M* concentration of the agents. It was at this concentration that the greatest range of differentiation in growth and melanization could be observed with the naked eye. Unstained wet mounts of each culture (including controls) were prepared for light microscopy observations. *Figure* 3 illustrates the variation in overall morphology, growth density, and pigmentation of the inhibited cultures versus the control. The least growth and melanization were found in cultures exposed to agent A. In that case, both spores and filaments (hyphae) could be observed with the hyphae predominating. Agent B allowed for similar growth, but with greater evidence of thick-walled pigmented cells in hyphae. Cells from cultures containing agent C were often swollen, thick-walled, and heavily pigmented, although overall growth was less than that of non-inhibited

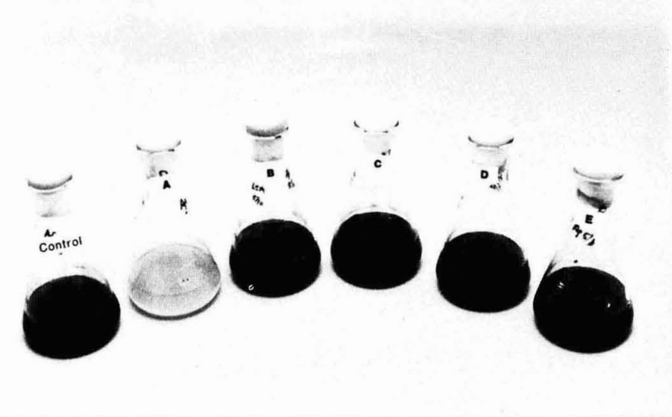

Figure 2—Flask cultures of *A. pullulans* at 72 hr post-inhibition (96 hr total growth). All are as heavily-pigmented as control (no inhibitor added) except the flask containing agent A

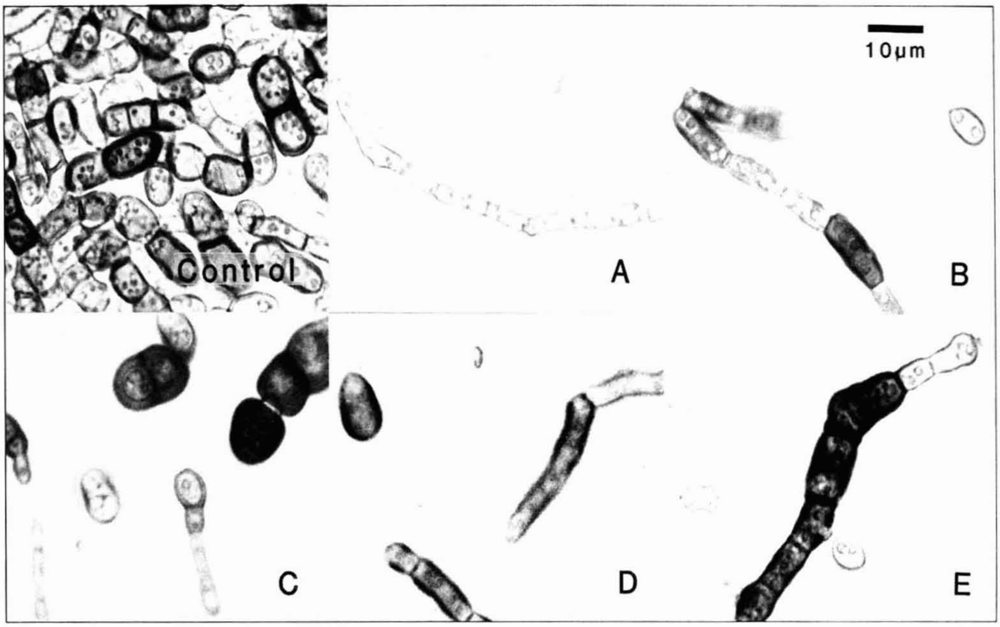

Figure 3—Light microscopy of *A. pullulans* control (upper left panel) culture at 72 hr post-inoculation, and treated cultures at 48 hr post-inhibition (72 hr total growth time). Letter designates the treatment. All treated cultures, although frequently heavily-pigmented, showed more sparse growth. All magnifications are identical and indicated by the bar line in the figure

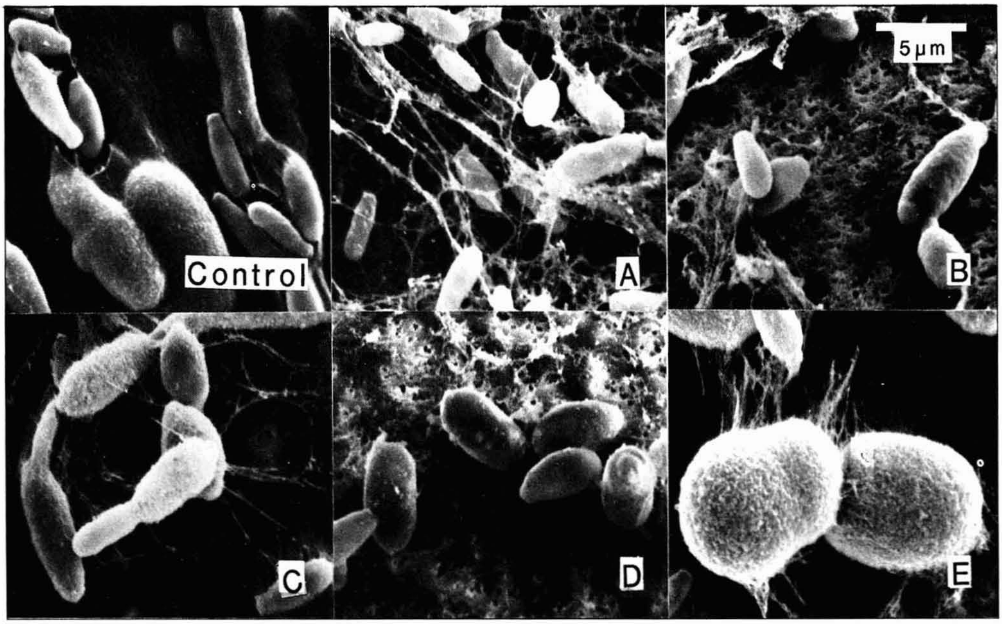

Figure 4—Scanning electron microscopy of cells from cultures grown as indicated in Figure 3. Extracellular web of cell extrusions is evident to varying degree in all treated cultures. Melanization of the cells correlates with the rough exterior of swollen cells

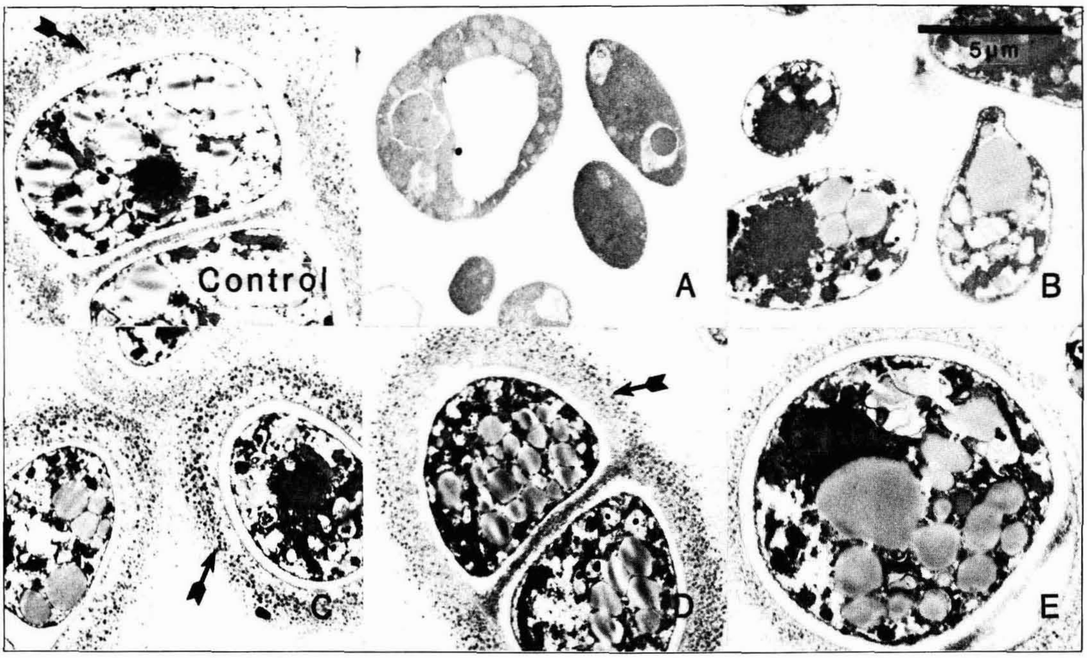

Figure 5—Low magnification transmission electron microscopy of sectioned *A. pullulans* control and the various indicated treatments. Extracellular melanization appears as dense surface granules outside the cell walls (large arrows) and within crosswalls (small arrows). Lipid inclusions within cells appear as striated (medium-dense) vesicular bodies. See text and *Table* 3 for details of cell structure

(control) cultures. Cells grown in the presence of agent C showed the establishment of new growth more closely resembling that from control cultures. Inhibitor D cultures also showed both melanized swollen cells and hyphae. Agent E cultures showed sparse growth compared with controls, but the hyphae were often swollen, dense, and possessed dark deposits along the cell walls.

In order to reveal greater detail of the surface structures of these cells than that obtainable with light microscopy, scanning electron microscopy (SEM) of portions of the same cultures was also performed. *Figure* 4 illustrates some views (all at the same magnification) of the control and the various inhibited cultures. A web-like sheath of extruded cellular material is evident in all inhibited cultures except D where only minor extrusion could be found. This material cannot be visualized with light microscopy and, although most likely present *in vivo,* may be an artifact of the preparation method. However, if an artifact, it could be due to weakened cell walls or solubilization of some wall component induced by the inhibitory treatment. The rougher cell surfaces in those cells exposed to agents C and E essentially correlate with the light microscopy observations of thickened cell walls with deposits. Due to the nature of the imaging, scanning electron micrographs often show dense surface structures as appearing light instead of their natural dark pigmentation which is observed visually.

Thin-section preparations for transmission electron microscopy (TEM) are illustrated in *Figure* 5 at low magnifications which permitted the observation of entire cell sections. The internal morphology of *A. pullulans* observed with TEM is considerably more complex than that indicated by the external appearance.[3] All cells are bounded by an outer wall which is relatively translucent to the electron beam. The control culture, as well as those from treatments C, D, and E all show varying amounts of dark melanin granules outside the cell wall and in interstitial regions of the crosswalls. Cells from all growth conditions exhibit lipid inclusions (medium-dense globular bodies within the cells), and small dense spherical bodies which have previously been demonstrated to be sites of polyphosphates.[4] Details of cellular organization could be observed at higher magnifications and are summarized in *Table* 3. Cell wall structure of affected *A. pullulans* cells was evaluated using density and thickness as compared with control cells. Cell membrane organization was evaluated as to whether there were swollen, disrupted, or completely lacking intact membranes at the cell surface or in the organelle structure. Extracellular deposits were generally presumed to be melanin pigments, but also included any evident dense secretions. The web-like materials captured by means of SEM were evidently lost in the more elaborate specimen preparation for TEM. The ability to identify organelles, such as mitochondria, was taken as the criterion of organelle integrity. Overall cellular integrity was determined by the presence of recognizable and intact structure in the cytoplasm with no loss of normal density. The degree of melanization was determined subjectively by the relative abundance of extracellular pigment granules. Cytoplasmic melanization was not considered since in most cases it appeared to be insignificant.

Table 3—Summary of 48 hr Post-Inhibitory Exposure of *A. pullulans* to 10^{-4} *M* Concentrations In LSM Observations with TEM as Compared with Control Cells. See Text for Definitions

Tests	A	B	C	D	E
Cell wall structure	Translucent	Thin	Normal	Normal	Normal
Cell membrane organization	Degraded	Disrupted	Normal	Normal	Disrupted
Extracellular deposits	Absent	Sparse	Present	Present	Present
Organelle integrity	Lacking	Lacking	Good	Disrupted	Lacking
Overall cell integrity	Poor	Poor	Fair	Fair	Fair
Degree of melanization	Lacking	Lacking	High	High	Medium

Although all cultures of *A. pullulans* prepared for microscopy in this study were believed to be pure, occasional bacterial contamination in some of the samples could be found. In those cases, this was traced to bottles of the inhibitors received several months earlier from manufacturers. The bacteria in all cases were cocci, between 0.5 and 1.0 μm diameter, motile, gram negative, and either requiring little free oxygen, or capable of surviving without air. Their effect on fungal growth and mildewcide molecular structure is unknown. They were found primarily in stocks of agents B and E, and to a lesser extent in A and C.

DISCUSSION

The finding that at low concentration, most inhibitors tested would tend to promote pigment production (melanization) may be a matter of some realistic concern in the weathering of coatings applications with incorporated mildewcides. As leaching occurs, the residual mildewcide could possibly serve as a stimulus for melanization through antagonistic properties. The inhibitors in general were most effective at concentrations above 1 × 10^{-4} *M*. Thus, it is important in the culture media employed (and presumably in any coatings formulation) to maintain a high level of mildewcide activity.

DR. RICHARD E. CRANG is a Professor of Plant Biology at the University of Illinois at Urbana-Champaign and Director of the Center for Electron Microscopy. He has published many papers on electron microscopy studies of organisms affected by environmental agents, and has been particularly concerned with research into the growth and inhibition of *Aureobasidium pullulans* and other paint-defacing mildews. Dr. Crang is PRI contractor and has worked closely with the coatings industry for several years.

SUSAN G. ROBINSON is a PRI investigator currently working on zinc and copper-containing mildew inhibitors incorporated into paint formulations. She is a graduate of Michigan State University in microbiology and has previously worked with the Environmental Research Laboratory at the University of Illinois at Urbana-Champaign.

The substantial variation in morphology, growth density, and pigmentation of the inhibited cultures is a strong indication that the mode of action of the various mildewcides tested is not the same. Some agents (e.g. A and B) inhibited wall development and melanization, whereas all but agent C disrupted or degraded recognizable organelle structures. While organelle integrity is closely bound to cellular membrane organization, the membranes may be intact but organelles may not be recognizable on a morphological basis (e.g. agent D). Extracellular pigmentation is, in general, closely related to the normal development of the cell walls. Agent E, however, indicated a partial inhibition of melanization with otherwise typically normal appearing cell walls. Inhibition of melanization is significant as it has been demonstrated that blocking its synthesis effectively controls growth in certain fungi.[5,6] The melanization process begins with the cytoplasmic secretion of low molecular weight biochemical pigment precursors. These precursors are transported into the region of the wall where the final oxidative and polymerization steps occur, which culminate in the morphologically distinct black pigment granules. In mammalian systems such precursors are generally tyrosine, but in the case of the fungi these compounds are typically phenolic. It is therefore possible that in the case of agent E, some interference may occur in the biosynthesis of melanin without necessarily being confined to the wall or its associated enzymes. Clearly, no inhibition of melanin took place with agents C or D and, in fact, a stimulation resulting in increased pigment production appears to have occurred.

Web-like extracellular materials may be the remnants of an enveloping protective sheath often found in *A. pullulans* cells during the early stages of growth.[2] Inhibitors may interfere with carbon substrate (sugar) metabolism which results in only partial production of the sheath. It has been shown that carbon and nitrogen sources as well as pH, aeration, and temperature can influence the production of extracellular polysaccharide termed "pullulan" in *A. pullulans.*[7,8] An enveloping sheath helps prevent dessication of the young cells, provides a matrix in which extracellular enzymes may function to degrade nutrient substrate materials, and prevents competitive microorganisms from obtaining a successful niche in the microenvironment. All of the inhibitors tested were successful in producing the sheath reduction, especially agent D.

It is of particular note that bacterial growth could be documented in the packaged inhibitors—most notably agents B and E. Not only does this bacterial contamination indicate the lack of broad-spectrum microbial inhibition, but it suggests the probability that the inhibitory agents themselves may be degraded by the bacteria. Such degradation could further render the inhibitors as being less than fully potent as mildewcide agents by the time of application. Alternatively, the agents in which bacterial growth can be found are most likely biodegradable—a clear, long-term advantage in matters of environmental concern. However, the time in which degradation occurs has not been documented. Further studies should be conducted on the microbial degradation of these and other prospective mildewcides considered for commercial usage.

SUMMARY

Unlike field testing, laboratory tests on the efficacy of mildewcides can reveal a variety of biological responses of fungi to inhibitory agents. In our observations it is clear that all inhibitory agents must be maintained at a high dose level to be effective (equal to or greater than 1×10^{-3} *M* concentration). The use of microscopic techniques for evaluating inhibitory responses yields information which discriminates between physiological effects of inhibitory agents on mildew organisms. The differences in efficacy noted in this study has led us to evaluate the relative effectiveness of the five inhibitors examined to be (from most effective to least effective): A, B, E, D, and C. Obviously, the complex factors associated with coatings formulations, application, and weathering (as in field testing) may significantly influence the relative efficacy of the five inhibitors reported in this study. However, these results are of particular value in relating the direct biological responses of the black mildew, *A. pullulans,* to inhibitory agents in LSM and which may extend to other substrates.

ACKNOWLEDGMENTS

This study was supported by a grant from the Paint Research Institute Mildew Consortium. The authors wish to acknowledge the assistance of the following firms in providing testing samples of inhibitors: Buckman Laboratories, Inc., Memphis, TN; Chapman Chemical Co., Memphis; Merck Chemical Div., Merck & Co., Inc., Rahway, NJ; Rohm and Haas, Philadelphia, PA; and Troy Chemical Corp., Newark, NJ. Additional laboratory assistance was provided by Mr. Mark Hughes and Ms. Julie Goff.

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THIS PAPER WAS AWARDED THIRD PRIZE IN THE 1983 ROON AWARDS COMPETITION

Pigment Volume Concentration And an Interpretation Of the Oil Absorption of Pigments

H.F. Huisman
PD Magnetics B.V.*

A new description for the pigment volume concentration, PVC, is given. It is based on the average effective density of the aggregated particles as these particles are present, e.g. in dispersions, in coating layers, and in oil absorption pastes.

The average effective particle density can be measured by mercury porosimetry.

In this paper, the model is applied to pigment powder packings, e.g., bulk and tap densities, and to oil absorption pastes. For powder packings good agreement is obtained with model calculations. For oil absorptions, the mathematical description of the OA paste contains three contributions; these are: (1) the average effective particle density; (2) the packing of the particles; and (3) the wettability of the particles by the oil,

The contribution of the adsorbed oil layer is only of minor importance. It is shown that the generally accepted description for the oil absorption, e.g. as formulated by Stieg, is an extreme case of the model given in this paper.

This model clarifies why in the past it was not possible to solve the problem of how to adjust exactly the OA-measurements or the powder compaction to give pigments packings that correlate with CPVC's derived from actual paint results.

INTRODUCTION

Since the early development of magnetic tape there has been a discussion about the kind of particles that are present in a magnetic dispersion and in a magnetic coating layer. This discussion resembles the discussion about dispersion quality in the paint industry.

Dispersion quality is a very important factor in the performance of a pigment dispersion and of a pigmented coating layer. The statement is that a "partly" dispersed pigment will always lead to an inferior performance in comparison with the same system with good dispersed pigment. Dispersion quality or degree of dispersion is very difficult to define. A number of attempts have been made to define and to measure it. In every textbook about paint technology at least one chapter is devoted to assessment of pigment dispersion.[1,2]

There is no disagreement about the ultimate degree of dispersion being the state of completely separated single particles, as described by Asbeck.[3] This ideal state, however, is hardly ever reached for normal inorganic pigments.

This is confirmed by many electron microscope pictures taken of particles in a good dispersion[2,5] and by particle size analysis of dispersions.[6] Only with rather coarse primary particles, i.e., those characterized by a BET surface area of a few m^2/g or less, can a dispersion process lead to that ideal situation.

The preparation of inorganic pigments often contains a process step in which the small primary particles are forced to cluster. This step is necessary for making the particles somewhat bigger so they can be separated economically[7] to obtain dry pigment powders. It is known that flocculated hydrophobic colloids can return to the original, completely dispersed state only under very special conditions, which are rare in practice.[8-10] This means the primary particles in the pigment powders are aggregated* by rather strong forces, and a complete disintegration of the pigment powder particles into primary particles is very unlikely if normal dispersion techniques are used.

Presented at the 61st Annual Meeting of the Federation of Societies for Coatings Technology in Montreal, Que., Canada, October 13, 1983.

*Molenstraat 37, 4902 NM Oosterhout, The Netherlands.

*By aggregates, we include all particles that are not single particles and held together by some force; we do not distinguish between aggregates, agglomerates, flocculates, clusters, etc.

The main reason for the ignorance of this situation is the difficulty of taking into account the presence of aggregated particles on a quantitative basis. Therefore, the most important assumption, that only primary particles are present, made in theories of interparticulate relationship is only a special case, and often invalid.

Theories in which particle packings, based on model calculations, are related with CPVC's in paint systems and with oil absorption values are especially faulty.[11-14] Fortunately, in a number of theories the prediction of CPVC's from particle packings involves oil absorption values as a starting point for the calculation and this, more or less, compensates for the effect of aggregates.[11,12] Oil absorption and pigment particles size data are used to calculate the thickness of the adsorbed oil layer. When doing so one does not find a constant layer thickness (within a factor of 2) as all adsorption theories predict; found are thicknesses that vary up to a factor of 20,[11] which is really unlikely.

To this general information, we add a few additional observations:

(1) Magnetic coatings were made with mixtures of magnetic pigments, 95% γ-Fe_2O_3 (Pfizer) and 5% CrO_2 (DuPont), according to our standard formulas and procedures. Small samples of these coatings were treated with HCl to extract the iron oxide. Whereas the CrO_2 is insoluble in HCl and the extraction time too short to degrade the polymer matrix a coating layer remains with a low concentration of CrO_2. Transmission electron microscope photographs taken from the extracted coatings show many small clusters of CrO_2 particles and only occasionally single particles.[15] This result indicates very strongly that the CrO_2 particles are present as clusters and that the clusters originate from the original powder and are not formed by flocculation in the pigment dispersion. A single CrO_2 particle has a 20 times greater chance of forming a cluster with γ-Fe_2O_3 particles than with other CrO_2 particles merely because of the volume concentration of the particles. This means that if in the dispersion process single particles have been formed then after extracting the γ-Fe_2O_3 only single and a few double CrO_2 particles would have been present, but this has not been found.

(2) The tensile properties of magnetic coating layers are routinely measured at PD Magnetics. If one plots the Young's modulus as a function of the pigment loading (% pigment γ-Fe_2O_3 on total solids on a weight basis) curves are obtained with the well known shape (examples in *Figure* 1). The maximum in this curve represents the critical pigment concentration (CPC). We have found by measuring the tensile properties of numerous pigment ladders that the CPC for systems with magnetic pigments hardly depends on the type of binders normally used for making magnetic coatings. It depends slightly on the dispersion agent. This statement is supported by the fact that different magnetic tapemakers working with the same magnetic pigments produce tapes which have electromagnetic performances within a very narrow regimen despite the tremendous differences in formulations and manufacturing procedures.

It is also supported by the experience that improvements of magnetic tapes, which have been seen over many decades, originate from the improvement in pigments more than anything else. If one compares the CPC for different magnetic oxides it can vary from 50 up to 80% (w/w). This is difficult to understand if one accepts the primary particles assumption, because all iron oxide particles have the same specific gravity (4.5 g/cm^3); roughly the same size and shape and the surface characteristics are very similar. By transforming the weight concentration into a volume concentration by taking into account the densities of the materials involved CPVC's of 20 to 50% are obtained. These are low values if they are compared with calculated packing factors for

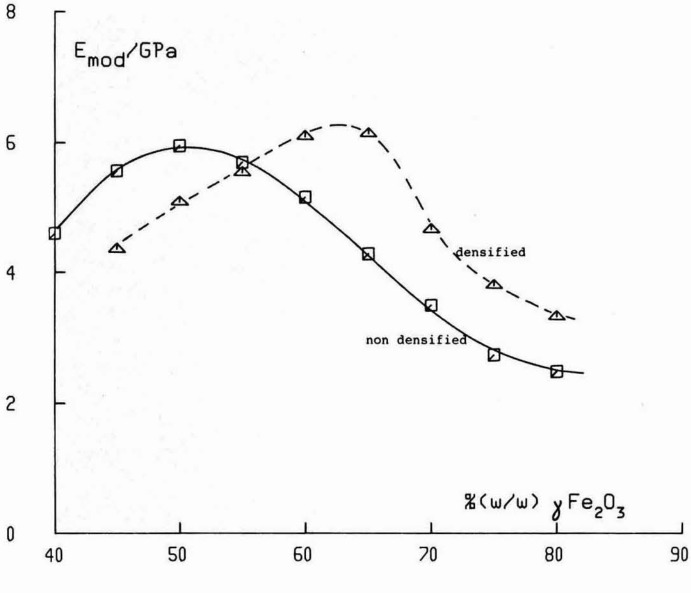

Figure 1—Young's modulus versus pigment loading for a normal and a densified magnetic iron oxide

these kind of systems. It becomes even more remarkable for densified pigments. In *Figure* 1 the curves for a normal pigment and the densified version are shown. The nondensified material has a CPC of 50% (w/w); the very same material has a CPC of 65% (w/w) after densifying it with a roll mill.

This is even more difficult to understand accepting the single particle assumption. It may even be expected that the more open structures of the nondensified material are easier to disperse than the densified structures, but the opposite seems to be true. It has been postulated that changes in the surface state are responsible for this effect.[16,17] However, this postulate is very unlikely because the changes in CPC's are so tremendous that very thick adsorbed layers have to be assumed. Further, ESCA measurement of the particle surface before and after densification shows only minor changes. This is confirmed by the adsorption characteristics of the powders.[15]

An obvious explanation for this behavior is the presence of aggregates and that these aggregates have a higher density in the densified powder than in the nondensified powder, and after dispersion of these powders this difference in density or part of it still exists.

All these observations lead to a model of a pigmented coating layer.

MODEL FOR PIGMENTED COATING LAYERS

A pigment dispersion and a pigmented coating layer is assumed to be built up from a heterodisperse system of aggregated particles which in many cases originate from the original powder particles. The model does not change if the aggregated particles are formed from smaller ones in the dispersion. The volume fraction of the pigment can be calculated if we define an average effective particle density of the aggregates, d_{agg}. The effective particle density is calculated from the weight of the aggregated particle and the aggregate volume. In the experimental part it is shown how this aggregate volume can be determined. Conceptually, it may be taken as the volume of the particle as defined, for example, by wrapping a thin elastic skin around the particle.

The equation for the volume, V (m^3), of 1 kg of coating layer then becomes

$$V = \frac{G_p}{d_{agg}} + \frac{1 - G_p}{d_b} \left\{ 1 - f \left(\frac{1}{d_{agg}} - \frac{1}{d_p^o} \right) G_p . \frac{d_b}{1 - G_p} \right\} + V_{Por} \quad (1)$$

G_p = weight of pigment in 1 kg of coating layer [kg]
$1 - G_p$ = weight of the rest of solid material, binders, dispersant, plastisizer, and other additives [kg]
d_{agg} = average effective particle density of the aggregated particles [kg/m^3]
d_b = density of the rest of the coating (minus pigment and voids) [kg/m^3]
d_p^0 = specific gravity of the pigment [kg/m^3]
f = proportionally constant; a measure for the fraction of the pores in the aggregates that is filled with binder
V_{Por} = pore volume between the aggregated particles

The first term of equation (1) represents the effective volume of the pigment. The second term is the volume of the binder in the interparticle space, therefore, the total amount of binder present is corrected by means of the f-factor for the amount that is in the "pores" of the pigment aggregates. Although in the present situation and for interpreting the data given in this paper a detailed description of the factors that control the amount of binder in the pores of the aggregates is not absolutely necessary, it seems logical that the following factors determine the f-factor:

(1) The total amount and the size distribution of the pores in the aggregated pigment particles.

(2) The total amount of binder present, and the binder concentration at the moment the coating layer solidifies.

(3) The wetting characteristics of pigment and binder.

In a forthcoming publication[18] the f-factor will be discussed in more detail.

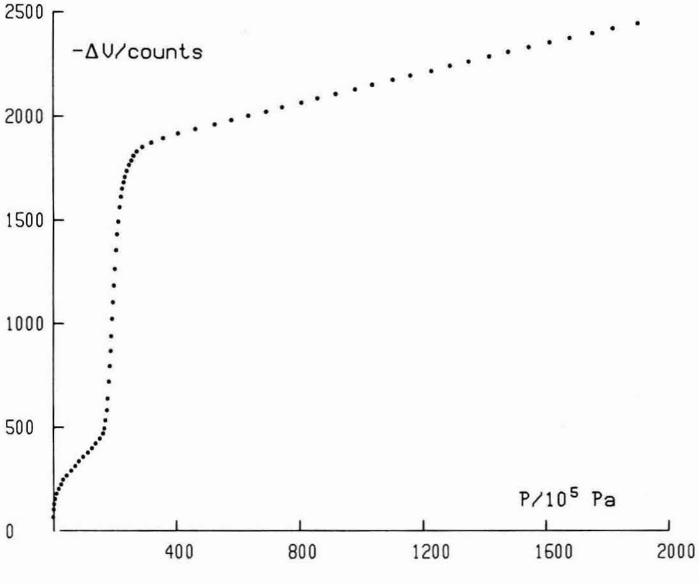

Figure 2—Typical porosimeter plot showing volume change versus pressure

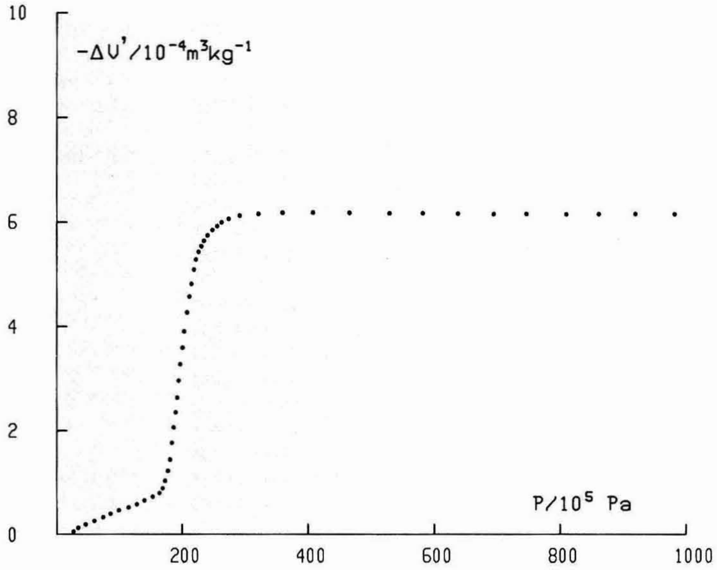

Figure 3—Typical plot of the corrected volume change versus pressure

The third term, V_{por}, is the pore volume between the aggregated particles, and is zero up to the critical pigment volume concentration. Above the CPVC, the term has to be taken into account.

In equation (1) the effect of the adsorbed binder layer is neglected. Because we assume the particles to be aggregated, they are much bigger than the primary particles and, consequently, the effect of the adsorbed layer is of less importance.[19] Further, the main surface area is inside the aggregated particles and the main part of the adsorbed material is already taken into account by the wettability factor, f. If, however, analysis shows that the aggregated particles are small the adsorbed layer can contribute substantially to the effective pigment volume. However, this contribution can only be calculated if the actual particle size (and distribution) and the thickness of the adsorbed layer are known.[19] Unfortunately, this is mostly not the case. With equation (1) for the volume of 1 kg of coating layer, the effective pigment concentration (PC) and the effective pigment volume concentration (PVC) can be calculated. These are, respectively:

$$PC = \frac{G_p}{V} = \frac{G_p}{\frac{G_p}{d_{agg}} + \frac{1-G_p}{d_b}\left\{1 - f\left(\frac{1}{d_{agg}} - \frac{1}{d_p^o}\right)\frac{G_p \cdot d_b}{1-G_p}\right\} + V_{por}} \quad (2)$$

and

$$PVC = \frac{G_p/d_{agg}}{V} = \frac{G_p/d_{agg}}{\frac{G_p}{d_{agg}} + \frac{1-G_p}{d_b}\left\{1 - f\left(\frac{1}{d_{agg}} - \frac{1}{d_p^o}\right)\frac{G_p \cdot d_b}{1-G_p}\right\} + V_{por}} \quad (3)$$

Most properties of coating layers are either related with PC or with PVC. Because the CPVC corresponds to the pigment volume concentration at which the binder just fills the voids between the packed pigment particles,[20] V_{por} is zero. This does not always mean that below the CPVC there is no porosity; this depends on the wettability factor, f. When $f = 1$, the interparticle pores are filled with binder; below the CPVC there is no porosity in the system. However, if $f \neq 1$, the voids in the aggregated particles are not filled completely with binder and the system is porous below the CPVC.

The same formulas can be used to describe mathematically the pigment concentrations in dispersions. In this case, the interparticle porosity, V_{por}, is of course, zero, but the pores in the aggregated particles are not necessarily filled. If the particles are not completely wetted, $f \neq 1$, the system contains a certain amount of air. This situation often occurs in the early stages of the dispersion process. Not only can pigmented coating layers and pigment dispersions be described with these formulas but any packing of particulate matter: apparent densities and tap densities of pigment powders and oil absorptions are examples. In all these situations the average effective particle density of the aggregates is the important property. This property can be measured via mercury porsosimetry.

APPLICATIONS

As mentioned, equation (3) can be used to describe mathematically pigment volume concentrations in pigment dispersions, in pigmented coating layers, in oil absorption pastes, and in pigment powder packings. In this paper we shall apply equation (3) to bulk and tap density powder packings and to oil absorption pastes. In a forthcoming paper the other systems, pigment dispersions, and pigmented coating layers will be discussed.

EXPERIMENTAL

Particle density data for pigment powders were obtained with a mercury porosimeter.* Details of the

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*In principle N_2 or Ar condensation (BET technique) may be used too.[21]

Table 1—Sources and Characteristics of Pigments

Sample	d_{agg} [g/cm³]	d_{app} [g/cm³]	d_{tap} [g/cm³]	ϕ_{app}	ϕ_{tap}	Notes
LMP 122	0.68^{5}	0.35	0.44	0.51	0.64	1
LMP 123	0.68	0.37	0.42	0.54	0.62	1
LMP 125	0.76	0.33	0.37	0.43	0.49	1
LMP 126	0.87	0.39	0.45	0.45	0.52	1
LMP 192	1.09	0.51	0.57	0.47	0.52	1
LMP 194	0.70	0.31	0.35	0.44	0.50	1
LMP 195	0.77	0.37	0.42	0.48	0.55	1
LMP 206	1.04	0.54	0.63	0.52	0.61	1
LMP 208	1.16	0.56	0.62	0.48	0.53	1
LMP 209	0.93	0.43	0.49	0.46	0.53	1
LMP 210	1.28	0.59	0.68	0.46	0.53	1
LMP 213	1.48	0.68	0.81	0.46	0.55	1
LMP 214	1.07	0.48	0.54	0.45	0.50	1
LMP 215	1.01	0.48	0.53	0.48	0.52	1
LMP 221	1.08	0.61	0.68	0.56	0.63	1
LMP 260	0.87^{8}	0.41	0.46	0.47	0.52	1
LMP 223	1.36	0.65	0.77	0.48	0.57	1
MP 580-258	0.88	0.45	0.50	0.51	0.57	2
MP 3870	0.76	0.35	0.40	0.46	0.53	2
MP 3156-	1.00	0.49	0.57	0.49	0.57	2
MP 172-054	0.60	0.32	0.36	0.53	0.60	2
AC 5099	1.67	0.86	0.98	0.51	0.59	3
MO 2228 Hc	1.28^{5}	0.64	0.79	0.50	0.58	4
LMP 307	0.71	0.35	0.40	0.49	0.56	1
BASF AMP	0.97	0.52	0.60	0.54	0.62	5
Bayer AC 3150M	1.76	0.98	1.07	0.56	0.61	6
MG 408	0.83^{5}	0.46	0.53	0.55	0.63	7
MG 408α	0.87	0.40	0.45	0.46	0.52	7
MG 409	1.01	0.53	0.66	0.52	0.65	7
MG 409α	0.94^{5}	0.45	0.50	0.48	0.53	7
P 678 B	0.76	0.36	—	0.47		7
P 678 BE γ01	0.69	0.36	0.42	0.52	0.61	8

Sample	d_{agg}/ g/cm⁻³	d_{bulk} g/cm⁻³	d_{tap}/ g/cm⁻³	ϕ_{bulk}	ϕ_{tap}	Notes
LMP 261	0.96	0.48	0.55	0.50	0.58	1
LMP 269	0.81	0.40	0.45	0.49	0.55	1
LMP 260	0.88	0.41	0.46	0.47	0.52	1
LMP 263	0.86	0.42	0.47	0.49	0.55	1
LMP 268	0.85	0.42	0.48	0.49	0.57	1
LMP 243	0.68	0.34	0.38	0.50	0.56	1
LMP 272	0.93	0.47	0.53	0.51	0.57	1
LMP 286	0.85	0.46	0.52	0.54	0.61	1
LMP 293	1.02	0.56	0.61	0.55	0.60	1
LMP 290	0.87	0.46	0.53	0.53	0.61	1
LMP 289	1.04	0.58	0.64	0.56	0.62	1
Hercules 1200 D	0.87	0.48	0.58	0.55	0.67	9
Pfizer RX 2581	1.36	0.64	0.93	0.47	0.68	10
BASF 2908 M	0.85	0.52	0.59	0.61	0.69	5
Al_2O_3 Alcoa	1.63	0.88	1.09	0.54	0.67	11
Syloid 244	0.25	0.08	0.10	—	—	12
T_iO_2	1.77	0.83	1.18	0.48	0.67	13
Cr_2O_3 Hercules	1.07	0.49	0.71	0.47	0.66	14
CrO_2 DuPont	1.51	0.70	0.95	0.46	0.63	15

Notes

(1) Experimental magnetic metal powders made on pilotscale by PD Magnetics. Specific surfaces area between 15 and 40 m²/g.
(2) Production magnetic metal powders made by PD Magnetics Specific surfaces areas 20 ± 2 m²/g.
(3) Magnetic γFe_2O_3 made by Bayer.
(4) Magnetic γFe_2O_3 made by Hercules.
(5) Experimental magnetic metal powder made by BASF.
(6) Experimental magnetic metal powder made by Bayer.
(7) Experimental goethites and α-Fe_2O_3's made by PD Magnetics.
(8) Magnetic iron oxides made by PD Magnetics.
(9) Magnetic metal powder made by Hercules.
(10) Magnetic metal powder made by Pfizer.
(11) Al_2O_3 A-3 made by Alcoa.
(12) Silica made by W.R. Grace and Co. The aggregate density is too high. Pores are not filled at highest pressure.
(13) TiO_2 type RLK made by Kronos.
(14) Cr_2O_3 made by Hercules.
(15) Magnetic CrO_2 type A made by DuPont.

equipment, the measuring procedure and the evaluation of the data were described earlier.[22] The porosimeter, an improved Carlo Erba type 200 apparatus, is controlled by a Philips minicomputer and produces a plot, illustrated in *Figure* 2, showing volume change as a function of applied pressure. The minicomputer corrects the data for the compressibilities of mercury and sample cell and calculates the pore volume in the aggregated particles, PV. A typical corrected curve is shown in *Figure* 3. The average effective particle density, d_{agg}, is calculated from the pore volume, PV and the specific gravity of the sample, d_p^o, with

$$d_{agg} = \frac{1}{PV + 1/d_p^o} \tag{4}$$

The average effective particle density of the pigment in the OA paste is also determined by intrusion porosimetry. This is done after reclaiming the pigment from the OA paste, either by extraction of nonvolatile oils or by evaporation if the "oil" is volatile.

Tubes, sealed on both ends with "Millipore" filters (Fluorpore: size 0.2 μ), were used for the extraction of oil. The tube with a few grams of the OA paste was placed in a Soxhlett apparatus and extracted with THF until the weight, after drying, was constant and all oil removed.

MATERIALS

All pigment powders were used as received. The magnetic pigments came from either commercial sources or were made by PD Magnetics. All nonmagnetic pigments were from commercial sources. The sources and main characteristics of the pigments are given in *Table* 1.

The linseed oil and the dibutylphlhalate were as described in the ASTM methods for the measuring of OA valves. All organic solvents were distilled before use.

Bulk and Tap Densities of Pigment Powders

The bulk density (d_B) is calculated from the volume (V_B) measured after standard filling of the sample vessel with 1 kg of powder, and the tap density (d_T) from the volume (V_T) after filling and tapping the sample vessel under controlled and prescribed conditions.[23]

If we assume that in both experiments the powder particles are not changed or damaged, the ratios of bulk and tap density with effective particle density, d_{agg}, are the respective volume packing factors for the powder in loose and dense random packing, ϕ_B and ϕ_T, expressed in the formulas:

$$\phi_B = d_B / d_{agg} \tag{5}$$

and

$$\phi_T = d_T / d_{agg} \tag{6}$$

The effective particle densities of about 50 magnetic and nonmagnetic powders were measured according to the procedures described in the experimental part. The values of d_{agg}, d_B, ϕ_b, d_T and ϕ_T are given in *Table* 1. In *Figure* 4 the bulk densities of all measured powders are plotted versus the effective particle density.

The linear regression equation that fits the experimental data best is:

$$d_B = 0.50\ d_{agg} - 0.002 \tag{5A}$$

with a coefficient of regression (r) of 0.98 and a standard error of estimate (s) of 0.04. Volume packing factors for loose random packing for these powders are between 0.59 and 0.43

In *Figure* 5 the tap density is plotted versus the effective particle density for the same powders. The linear regression equation that fits best is:

$$d_T = 0.59\ d_{agg} - 0.006 \tag{6A}$$

with a coefficient of regression of 0.98 and a standard error of estimate of 0.04. The volume packings are between 0.50 and 0.67 with a mean value of 0.59. Both the intercepts of equations (5A) and (6A), −0.002 and −0.006, are not significantly different from zero.

Equations (5) and (6) are simplifications of equation (3) if this equation is adapted to powder packings (ϕ = PVC). The average value, 0.59, for the volume packing of the powder particles in the tap density experiments is a value by chance and is brought about by the fortuitous selection of the powders. It means that every value of ϕ_T has a unique meaning and is determined by the size, the size distribution, and the shape of the powder particles.

For special situations, ϕ can be calculated, e.g., for loose and dense packing of uniform spheres, or for spherical particles with a continuous size distribution. For the last situation, Lee[24] found theoretically a packing factor of 0.69. This value is in good agreement with the highest values, 0.67 − 0.69, found for the volume packing of magnetic powders, which were produced in a fluid bed reactor. The lower values are for powders with less spherical or very small particles.

Measuring effective particle density of powders by means of mercury intrusion measurements is an easy way of determining packing factors for the different powders packings, and in combination with tap density characterizes a pigment powder.

Oil Absorptions

Oil absorption measurements are made so often because it is generally accepted that the OA data of a pigment and the CPVC of that pigment in a coating layer are related.[12,14] For the transformation of OA data into CPVC data it is assumed that the pigment is in the state of completely separated single particles and that the pigment packing is the same in both situations. However, the argument for the presence of aggregated particles in paints is even more justified for OA pastes taking into account the short time an OA measurement takes compared with the dispersion time of a pigment in paint production. This means that the presence of aggregated

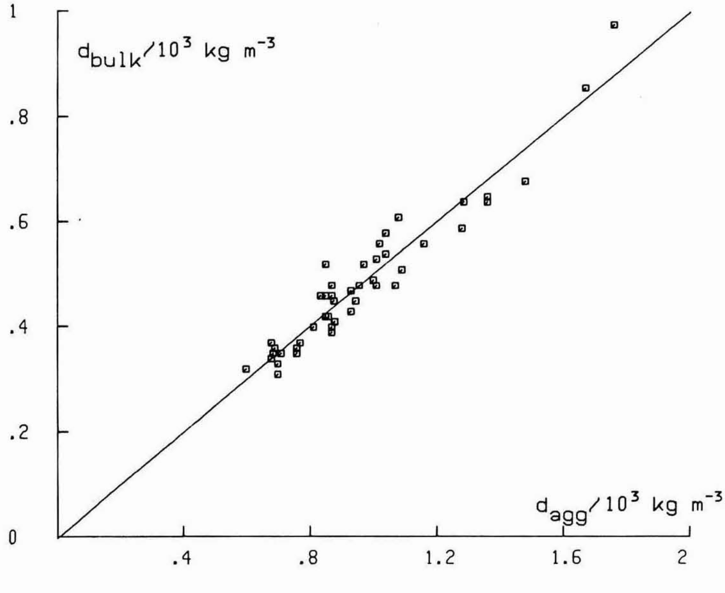

Figure 4—Bulk density of magnetic and non magnetic powders versus the average effective particle density

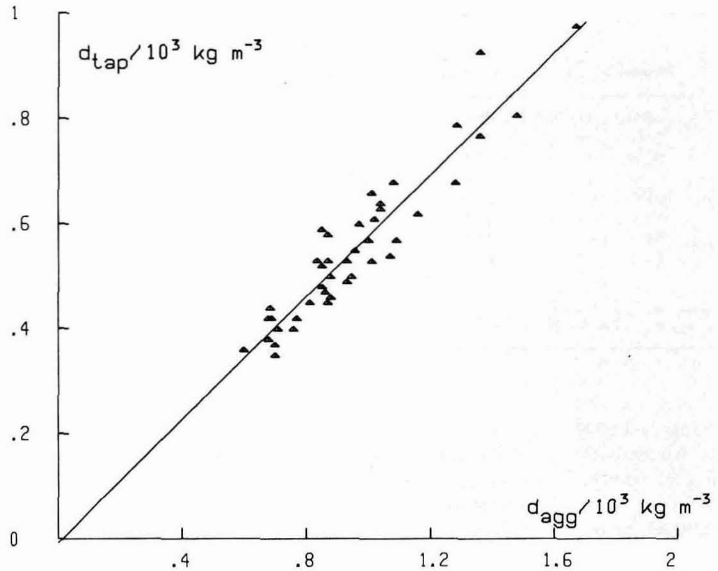

Figure 5—Tap density of the powders of Figure 4 versus the average effective particle density

particles has to be taken into account by adapting equation (3) to the OA end point paste.

This gives:

$$\phi_f^{OA} = CPVC_{OA} = \frac{100/d_{agg}^{OA}}{100/d_{agg}^{OA} + OA - f\left(\frac{1}{d_{agg}^{OA}} - \frac{1}{d_p^o}\right)100} \quad (7)$$

ϕ_f^{OA} = The effective volume packing factor of the pigment in the OA paste
d_{agg}^{OA} = Average effective particle density of the pigment
OA = *Volume of oil per 100 g pigment*
f = Wettability factor

As in equation (3), the effect of adsorbed layers is neglected. If the particle size distribution of particles in the OA paste is known, the correction for the adsorbed layers on the packing factor can be made.[19]

Equation (7) contains two variables, d_{agg}^{OA} and f, which completely control the OA end point. The effective particle density, d_{agg}^{OA}, can vary between two extremes: d_p^o to d_{agg}^{powder}.

(a) $d_{agg}^{OA} = d_p^o$. This means the particles are completely separated and there are no aggregated particles present. Equation (7) becomes:

$$CPVC = \frac{100/d_p^o}{100/d_p^o + OA} \quad (8)$$

and is *identical to the Stieg equation.*[12,25]

(b) $d_{agg}^{OA} = d_{agg}^{powder}$. The average effective particle density of the powder is not changed by the OA experiment. This can only happen with particles that are strongly aggregated or sintered. In this case there is also a direct relation between OA and the reciprocal of the tap density of the powders.

In most cases, however, d_{agg}^{OA} has a value between the two extremes.

The second variable in equation (7) is the wettability factor, f. This factor can vary between 0 and 1. If f = 0, it means no intrusion of the oil into the pores of pigment aggregates and equation (7) becomes:

$$\phi_o^{OA} = \frac{100/d_{agg}^{OA}}{100/d_{agg}^{OA} + OA} \quad (9)$$

With f = 1, complete intrusion of the oil takes place and the packing factor becomes:

$$\phi_1^{OA} = \frac{100/d_{agg}^{OA}}{100/d_p^o + OA} \quad (10)$$

To use equation (7) one has to determine the two controlling variables. The wettability factor, f, can be determined by comparing the density of the OA paste with the density calculated from the weighted specific gravities of the composing materials, pigment and oil. The average effective particle density, d_{agg}^{OA}, can be *measured with intrusion porosimetry* after removing the oil from the paste.

FACTORS AFFECTING OIL ABSORPTION OF PIGMENTS

A few factors known to influence oil absorption values substantially were investigated.

Comparison Of the Spatula Rub Out And Coleman Gardner Method

The two methods give dissimilar OA values for all pigments. The SRO method (ASTM D 261-31) always leads to much lower OA-values than the C.G. method (ASTM D 1483-60). The difference is normally attributed to *the consistency of the paste at the end point.* To

Table 2—Comparison of Spatula Rub Out and Coleman Gardner Method

Sample	Oil	Method	OA [mL/100 g]	d_{agg}^{OA} [g/cm³]	f	ϕ_f^{OA}
γFe_2O_3[a]	Linseed	SRO	38.0	1.98	0.96	0.82
γFe_2O_3	Linseed	C-G	49.0	1.81	1	0.77
γFe_2O_3	DBP	SRO	50.5	1.70	0.98	0.81
γFe_2O_3	DBP	C-G	58.0	1.63	1	0.77
CrO_2[b]	Linseed	SRO	33.0	2.17	1	0.82
CrO_2	Linseed	C-G	48.5	1.87	1	0.77
CrO_2	DBP	SRO	49.0	1.65	0.90	0.82
CrO_2	DBP	C-G	60.5	1.55	0.94	0.77

(a) Effective particle density of the powder 1.49 g/cm³ spec. surface area 19 m²/g AC 5064 Bayer.
(b) Effective particle density of the powder 1.51 g/cm³ spec. surface area 22 m²/g CrO_2A DuPont.

investigate this behavior two magnetic pigments (γ-Fe_2O_3 and CrO_2) were measured according to the two methods using also two different oils, linseed oil and dibutylphthalate.

The procedures followed were as described in the ASTM methods. The results are in *Table* 2.

From these results the following conclusions can be drawn:

(a) Equation (7) describes the end point paste situation and leads to packing factors that are reasonable. The packing factors are relatively high but the OA paste is not representative for free settling pigment particles.

(b) The densification of the aggregated particles is higher for the SRO method than for the C.G. method. This can be understood from the energy that is put in.

(c) The packing of the particles in the SRO end point is somewhat higher than in the G.C. situation. In both situations the volume packing is independent of the wettability factor.

(d) Linseed oil is more effective in increasing the aggregate density than DBP. This may explain the general trend that DBP OA values are higher than the corresponding linseed values.[26] This difference may originate from the interaction energy between the pigment and the oil.

(e) DBP does not completely wet the CrO_2 particles. After longer times the OA pastes become dry and crumbly, indicating slow intrusion of DBP into the pores of the aggregates.

The difference between the two methods is based on two factors: the density of the aggregates and the packing of the particles.

The Operator Effect

In 1959 Marsden[27] concluded that the variability of oil absorption results are solely dependent upon the extent of rubbing by the operator. This conclusion was supported by a lot of his own experimental work and from results taken from literature.[28]

To investigate the operator effect, the results obtained with five different magnetic metal powders measured by two of our operators were analyzed. One of the operators always found lower OA values than the other one.

The mortar and pestle method was used for the measurement. Also, the pigments from the OA pastes were recovered by THF extraction and the effective particle density determined.

The results are in *Table* 3. Because we did not measure the density of the pastes, f could not be determined and the exact packing factors are unknown. Therefore the two extreme packing factors according to the equations (9)

Table 3—The Operator Effect

			Operator 1				Operator 2			
Sample[a]	d_{agg}^{P} [g/cm³]	S_A [m²/g]	OA [mL/100]	d_{agg}^{OA} [g/cm³]	ϕ_o^{OA} [eq.(9)]	ϕ_1^{OA} [eq. (10)]	OA [mL/100 g]	d_{agg}^{OA} [g/cm³]	ϕ_o^{OA} [eq. (9)]	ϕ_1^{OA} [eq. (10)]
LMP 121	1.21	22.1	63	1.50	0.51	0.85	66	1.42	0.52	0.86
LMP 122	0.68[5]	24.5	58	1.68	0.51	0.81	74	1.32	0.51	0.85
LMP 123	0.68	24.5	64	1.45	0.52	0.87	68	1.40	0.51	0.85
LMP 125	0.76	22.5	48	1.99	0.51	0.79	54	1.83	0.50	0.78
LMP 126	0.87	21.4	42	2.19	0.52	0.79	48	1.97	0.51	0.80
				Average:	0.51 ±0.01	0.83 ±0.04		Average:	0.51 ±0.01	0.83 ±0.04

(a) Metal powders made by PD Magnetics; spec. surface areas between 21 and 25 m²/g.

Table 4—Effect of the Rate of Addition of DBP on OA and Effective Particle Density

Time [min]	OA [mL/100 g]	d_{agg}^{OA} [g/cm³]	ϕ_o^{OA} (eq. (9))	ϕ^{OA} (eq. (10))	f	ϕ_f^{OA}
Sample			*AC 5099 M (Bayer)*[a]			
2.41	51.0^5	1.51	0.56	0.92	0.95	0.89
5.15	47.9	1.55	0.57	0.93	0.96	0.91
8.26	45.9	1.63	0.57	0.91	0.97	0.90
12.16	45.0	1.65	0.58	0.92	0.96	0.89
14.94	44.4	1.66^5	0.58	0.92	0.97	0.90
20.69	43.5	1.67^5	0.58	0.92	0.97	0.91
49.0	40.4	1.73	0.59	0.94	0.95	0.91
13.50[b]	29.4	2.15	0.61	0.92	0.98	0.91
Sample			*MO 2228 Hc (Pfizer)*[c]			
2.71	57.5	1.42	0.55	0.89	0.97	0.88
6.63	52.4	1.50	0.56	0.91	0.96	0.88
6.66	53.0	1.47	0.56	0.92	0.96	0.89
22.40	47.0^5	1.56	0.61	0.94	0.95	0.91
52	43.2	1.68	0.58	0.97	0.97	0.91

(a) Spec. surface area 23.5 m²/g, powder particle density 1.37 g/cm³.
(b) In this case the pigment is added to the oil. This point is not included in the analysis.
(c) Spec. surface area 23.0 m²/g, powder particle density 1.31 g/cm³.

and (10) were calculated. The average of the two packing factors for the five pigments are equal for both operators. This justifies the expectation that the real packing factors are also equal.

The difference between the two operators can be explained by differences in applied forces, which lead to a difference in densification of the aggregates in the OA pastes; this can also explain the findings of many others.[27,29,30]

One also sees that the differences between the two operators are not constant. This means that the procedure sometimes recommended to "calibrate" OA measurements[14] is not correct for these powders.

Instrumental Procedure For Determining OA Values

In a Roon Awards paper, Hays[26] discussed OA measuring methods and showed the advantages of using standardized equipment to eliminate the operator effect and the uncertainty in the end point. The Brabender Plasticorder is such an instrument. An effect, still present, is the rate of oil addition which has a noticeable effect on the OA values. Though Hays states that the OA's vary little above a certain mixing time, his measurements indicate a continuing decrease in OA values with increasing mixing time. This was also found by Wirsching and Haug.[31]

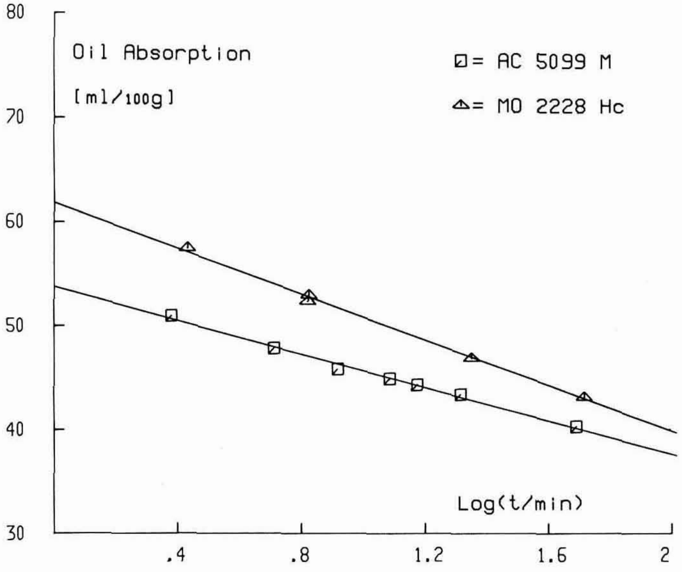

Figure 6—Oil absorptions of two magnetic iron oxides as function of mixing time in the Brabender Plasticorder

Table 5—Liquid Absorption of γ-Iron Oxide[a]

Liquid	OA [mL/100 g]	d_{agg}^{OA} [g/cm³]	ϕ_o^{OA} (eq. (9))	ϕ_1^{OA} (eq. (10))	f	ϕ_f^{OA}
Linseed oil	38	1.98	0.57	0.85	0.96	0.82
Cyclohexanone	45	1.83	0.54	0.82	1	0.82
Water	47	1.77	0.55	0.83	1	0.83
DBP	50.5	1.70	0.54	0.82	0.98	0.82
Ethyl glycol	49	1.76	0.54	0.81	0.96	0.79
Diisobutylketon	50.5	1.58	0.56	0.88	0.87	0.82
Ethylene diglycol	45.5	1.81	0.55	0.83	1.0	0.83
					Average ϕ_f^{OA}	0.82 ± 0.02

(a) AC 5099 M Bayer.

Therefore, we measured for two magnetic iron oxides from Bayer, AC 5099 M, and Pfizer, Mo 2228, the OA's as function of the rate of addition of DBP. The densities of the different OA pastes were measured and after reclaiming the pigments the average particle density was determined. The results are in *Table* 4. The OA data are plotted as function of mixing time (t) in *Figure* 6. The regression curves for the two oxides are, respectively:

$$OA = 53.7 - 7.9 \log t \qquad (11)$$

with a coefficient of regression (r) of 0.996 and a standard error of estimate(s) of 0.33,
and

$$OA = 61.9 - 11.0 \log t \qquad (12)$$

with

$$r = 0.998 \text{ and } s = 0.36.$$

The slopes of the curves have the same order of magnitude as found by Hays[26] and by Wirsching and Haug.[31] Increasing mixing time leads to increasing effective particle density and to lower absorption data. Further, there is a very slight increase in packing factor at decreasing addition rates. The packing factors are higher than with the other OA methods. This indicates that the aggregate shape adapts itself to the experimental conditions, and that the packing of the pigment particles in this experiment is far from a free settling situation as model calculations[24] assume.

Liquid Adsorption Of Different Types Of Organic Solvents

Liquid adsorption values for a pigment can differ substantially as different organic liquids are used.[32,39] A reasonable explanation for these differences has never been given, though there are found relations with other properties such as interfacial tension.[34]

To elucidate the liquid effect, liquid absorptions have been determined for two magnetic pigments with a series of different liquids by the SRO method (ASTM D 261-31). Corrections for evaporation were made by weighing. The densities of the pastes and the effective particle densities were measured in the usual way. The results are in *Tables* 5 and 6.

Also, here equation (7) gives a good description of the OA end points. The differences in "OA" values are caused by differences in the effective particle density, in other words, by differences in the degree of densification of the aggregates. In some cases there is also an effect of wettability.

The method is also applicable for non-magnetic pigments. Therefore, we measured the liquid absorption values for three magnetic pigments and compared them with the liquid absorptions for three different TiO_2's. For this procedure we used the Brabender Plasticorder. The

Table 6—Liquid Absorption of Chromium Dioxide[a]

Liquid	OA [mL/100 g]	d_{agg}^{OA} [g/cm³]	ϕ_o^{OA} (eq. (9))	ϕ_1^{OA} (eq. (10))	f	ϕ_f^{OA}
Linseed oil	33	2.17	0.53	0.82	1	0.82
Cyclohexanone	50	1.74	0.53	0.82	1	0.82
Water	42	1.97	0.55	0.82	1	0.82
DBP	49	1.65	0.55	0.88	0.90	0.83
Ethylglycol	45	1.83	0.53	0.84	0.95	0.82
DIBK	56	1.55	0.54	0.85	0.95	0.83
Ethylene diglycol	40.5	1.90	0.57	0.87	0.87	0.81
					Average ϕ_f^{OA}	0.82 ± 0.01

(a) CrO_2 A DuPont; spec. surface area 22 m²/g.

Table 7—Liquid Absorptions of γ-Fe_2O_3[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	d_{paste} [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	33.9	0.953	4.5	2.36	1	2.06	0.86
DBP	36.9	1.046	4.5	2.34	0.97	1.88	0.88
DIBK	39.7	0.804	4.5	2.05	0.93	1.81	0.86
Butylacetate	45.1	0.881	4.5	2.03	0.96	1.68	0.86
Cyclohexanon	36.1	0.945	4.5	2.28	1	1.91	0.90
DMF	32.7	0.946	4.5	2.24	0.88	1.95	0.88
Amylacetate	41.1	0.875	4.5	2.06	0.92	1.76	0.86
H_2O	36.6	0.998	4.5	2.30	0.98	1.93	0.87
						Average:	0.87 ± 0.02

(a) AC 5099 M Bayer.

rate of oil addition was 0.5 mL/min. The results are reported in *Tables* 7–12.

These tables show that the TiO_2 pigments do not behave differently from the magnetic pigments. The degree of densification is somewhat higher than for the magnetic pigments. This reflects the absence of magnetic forces for the TiO_2's. The contribution of the adsorption of oil on the pigments also seems to be negligible (with respect to the packing factors).

Comparison Between Compaction Of Powder and the SRO Method

Bassey and Lammiman[28] investigated the compaction of powders and powder-oil mixes and came to the conclusion that this method leads to the lowest OA values, which they called the "true" OA values. They used a mechanical compaction device, a cylinder with one plunger by which the powder was impacted. After 100 impacts the volume of 10 grams of powder (or powder-oil mix) was determined and the OA values calculated. Because the conditions for compacting were selected arbitrarily, optimization with respect to the application of the powder is obvious. E.v.d. Meulen[35] developed an alternative procedure which is easy to optimize with respect to the application of the powders he used. He constructed a die with two movable plungers with a narrow slit between the plungers and the cylinder wall through which the excess "oil" can escape if the pressure on the plungers increases.

From the volume versus pressure curve, the optimum composition of the paste, in which the powders are to be dispersed can be estimated with good accuracy. The empirical relation between volume pressure curve and paste composition was found after statistical analysis of many experiments.

For two magnetic metal powders, one "soft" and the other "hard," the volume of the wetted powder is measured at two pressures (1.10^7 and 5.10^7 Pa). The maximum pressure is maintained for 30 minutes after which the pressure is released and the volume and weight of the sample measured. The samples are pulverized after drying and the effective particle density determined. After reclaiming the pigment from the OA paste the effective particle density is also measured. The results are in *Table* 13.

The results show that it is possible to find pressure conditions which lead to the same "OA" values as measured by the normal SRO method. In our case this pressure is close to 5×10^7 Pa. Nevertheless, the actual situations in the OA paste and in the pressed cakes are completely different. For the pressures applied in these experiments, the effective particle densities are lower and

Table 8—Liquid Absorptions of CrO_2[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	d_{paste} [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	30.8	0.953	4.6	2.46	1	2.14	0.89
DBP	37	1.046	4.6	2.26	0.92	1.84	0.89
DIBK	34.3	0.803	4.6	2.23	0.96	1.97	0.89
Butylacetate	38.6	0.88	4.6	2.18	0.96	1.79	0.91
Cyclohexanon	37.2	0.944	4.6	2.23	1.0	1.90	0.90
DMF	33.8	0.947	4.6	2.38	1.0	2.05	0.88
Amylacetate	40.8	0.874	4.6	1.99	0.86	1.64	0.89
H_2O	25.8	0.998	4.6	2.65	1.0	2.34	0.90
						Average:	0.89 ± 0.01

(a) CrO_2 DuPont.

Table 9—Liquid Absorptions of LMP[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	d_{paste} [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	61.8	0.953	6.4	2.05	1	1.57	0.82
DBP	33.3	1.046	6.4	2.18	0.94	1.76	0.80
DIBK	60.8	0.803	6.4	1.95	1	1.64	0.80
Butylacetate	65	0.880	6.4	1.77	0.86	1.39	0.81
Cyclohexanon	59.4	0.995	6.4	1.96	0.91	1.54	0.82
DMF	69	0.994	6.4	1.96	1	1.50	0.79
Amylacetate	72	0.875	6.4	1.78	0.93	1.36	0.80
H_2O	65	0.998	6.4	1.93	0.91	1.96[b]	0.80
							0.81 ± 0.01

(a) Magnetic metal powder, made by PD Magnetics.
(b) MP/H_2O completely oxidated: PV 3.71×10^{-4} m³/kg after correction 5.30×10^{-4} m³/kg.

Table 10—Liquid Absorptions of TiO_2 Cl 300[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	d_{paste} [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	16.4	0.954	4.2	2.88	1	2.79	0.89
DBP	22.9	1.046	4.2	2.65	1	2.35	0.91
DIBK	23.1	0.804	4.2	2.53	1	2.40	0.89
Butylacetate	25.8	0.878	4.2	2.49	1	2.22	0.92
Cyclohexanon	23.0	0.945	4.2	2.60	1	2.40	0.89
DMF	20.2	0.947	4.2	2.68	0.97	2.49	0.90
Amylacetate	23.5	0.874	4.2	2.55	1	2.37	0.89
H_2O	18.4	0.998	4.2	2.71	0.91	2.49	0.92
						Average:	0.90 ± 0.01

(a) Kronos TiO_2; spec. surface area 13.8 m²/g.

Table 11—Liquid Absorptions of TiO_2 R 320[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	d_{paste} [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	18.8	0.954	4.2	2.68	0.91	2.51	0.91
DBP	26.0	1.046	4.2	2.49	0.94	2.14	0.91
DIBK	28.3	0.805	4.2	2.35	1.0	2.09	0.91
Butylacetate	35.0	0.88	4.2	2.18	0.96	1.88	0.89
Cyclohexanon	30.5	0.945	4.2	2.33	0.96	2.02	0.90
DMF	23.0	0.948	4.2	2.54	0.94	2.30	0.91
Amylacetate	31.3	0.873	4.2	2.30	0.99	2.03	0.89
H_2O	23.2	0.998	4.2	2.55	0.93	2.31	0.90
						Average:	0.90 ± 0.01

(a) Sachtleben TiO_2 spec. surface area 6.6 m²/g.

the packing factors are higher in the pressed cakes than in the OA pastes. It is clear from the results that the true oil absorption as a general phenomenon does not exist but is restricted to the powders which do not give aggregated particles, but can be treated as single particles. Bassey and Lammiman[28] both used ground natural materials, whitings and barytes; these are probably examples of powders giving such particles automatically leading to the lowest OA values.

Though true oil absorptions are restricted to special situations, it is, on the other hand, possible to adjust the compaction method to give "OA" values that correlate with the actual OA measurement. However, this adjustment must be determined for every pigment powder.

Table 12—Liquid Absorptions of TiO_2 LOCR[a]

Oil	OA [mL/100 g]	d_o^{oil} [g/cm³]	d_o^{pigm} [g/cm³]	dpaste [g/cm³]	f	d_{agg}^{OA} [g/cm³]	ϕ_f^{OA}
Linseed oil	25.5	0.995	3.8	2.38^5	0.98	2.10	0.91
DBP	37.8	1.046	3.8	2.17	1	1.75	0.89
DIBK	38.8	0.803	3.8	2.05	1	1.70	0.90
Butylacetate	43.1	0.880	3.8	1.98	1	1.63	0.88
Cyclohexanon	39.7	0.945	3.8	2.08	1	1.68	0.90
DMF	35.7	0.948	3.8	2.16	1	1.79	0.90
Amylacetate	43.2	0.879	3.8	1.99	1	1.62	0.89
H_2O	30.8	0.998	3.8	2.20	0.91	1.92	0.88
						Average:	0.89 ± 0.01

(a) Sachtleben TiO_2 LOCR; spec. surface area 8.6 m²/g.

DISCUSSION

According to the generally accepted description, sometimes with some doubts,[36] the oil absorption paste consists of dispersed single pigment particles, each having a layer of oil on its surface together with sufficient oil to fill the space between the particles which are assumed to be packed as dense as possible.

The description was converted into an equation by Stieg.[25]

$$\text{CPVC} \equiv \frac{P}{P + OA_V} = \frac{P}{P + a + b}$$

P = standard volume of pigment (Weight/d_p^o)
OA_V = volume of per standard volume of pigment
a = volume of adsorbed oil
b = volume of free oil

The value of b is a function of size distribution which determines the packing of particles and it can be calculated from model consideration.[11,24] While a is supposed to be a function of surface area and when expressed per unit area should have a constant value (at least within a factor of 2), in practice a varies tremendously, in contradiction with all existing adsorption theories. Although the adsorption correction, a, in Stieg's equation is theoretically correct, it can only be calculated from first principles if aggregated particles are absent.

In this situation, a is proportional to the specific surface area of the pigment. In all other cases it is proportional to the mostly unknown outer surface area of the aggregated particles.

This means that in normal situations the adsorption of oil onto the pigment hardly affects pigment packings. For small single particles where adsorption is important the forces that hold the aggregated particles together are relatively strong compared with the shear forces in the dispersion process. On the other hand for large single particles, of which one may expect that they can be separated in a dispersion process, the contribution of the adsorbed layer to the effective pigment volume is small.[19]

The introduction of the effective density of aggregated particles leads to a clear picture of oil adsorption. It also gives a very plausible explanation for many effects that have been discussion points for a long time or have not been explained at all. There are three effects that control the OA end point:

(a) *The effective particle density of the aggregates* in the OA end point paste, which depends on: The work done on the paste; The intrinsic properties of the powders, such as the strength of the aggregates; The size and size distribution, in combination with the particle shape; The specific gravity; The oil used; here the interfacial free energy between pigment surface and "oil" is probably the ruling property.[34]

(b) *The packing of the aggregates*, which depends on the method used and the work done on the paste. Due to the shearing action of most methods the packing of aggregated particles is much higher than in a free settling situation and is difficult to predict from model calculations.

(c) *The wettability of the pigment* aggregates by the "oil." In most cases the pigment is wetted by the oil

Table 13—Compaction Experiments with "Soft" and "Hard" Metal Powders

	MP 172 "Soft"[a]	MP 156 "Hard"[a]
Pressure: 1×10^7 Pa		
Volume [cm³] (under pressure)	1.675	2.33^5
"OA" calculated [mL/100 g]	66.7	96.5
Pressure: 5×10^7 Pa		
Volume [cm³] (under pressure)	1.117	1.492
OA calculated [mL/100 g]	38.8	54.3
Volume [cm³] (after pressure release)	1.180[b]	1.624[c]
"OA" measured [mL/100 g]	42.0	60.9
d_{agg} [g/cm³]	1.72	1.38
Packing factor	0.99	0.89
OA (SRO) [mL/100 g]	42.0	64.0
d_{agg}^{OA} [g/cm³]	2.02	1.50
Packing factor	0.84	0.79
d_{agg}^{powder} [g/cm³]	0.84	1.00

(a) Experimental magnetic metal powders PD Magnetics.
(b) The surface of the sample was smooth and glossy.
(c) The surface of the sample was rugged and dull.

completely. In two situations, however, wettability is not complete:

If the test is done very fast and the viscosity of the oil is high, wettability may not be complete. This phenomenon shows up by a relatively fast change in the consistency of the paste during standing; it becomes dry and crumbly.

And if the contact angle between powder and oil is finite. From equation (8) the effect of a finite contact angle arises naturally and confirms the findings of Bartell and Greager.[34]

This model also clarifies why it was not possible to solve the problem of how to exactly adjust the OA measurement or the powder compaction to give pigment packings that correlate with CPVC's derived from actual paint results.

This model of aggregated pigment particles in paints and in OA pastes has practical implications.

It is generally accepted that the CPVC of a pigment in a paint system and certain OA data are directly related.[11-13,25] However, in publications there has been expressed directly or indirectly some doubts about the correctness of this statement.[20,27,36,37] From the interpretation given in this paper it becomes clear that both situations can be correct, of course not at the same time. To have a direct relation between CPVC and OA data the pigment must either (1) be in a completely separated state; or, (2) have the same aggregate density and pigment packing in the paint and in the OA paste; or, (3) the two controlling effects (density and packing) lead in the two systems to the same end point (high density and low packing for one end point compared to lower density and higher packing in the other end point).

The first situation can occur with rather coarse primary particles,[25,38] the second situation is very unlikely as demonstrated in this paper, and the third situation is a matter of change and also not very likely but can be achieved deliberately. Consequently, for most practical applications it can be stated that a direct relation between CPVC and OA data is incorrect. This does not mean that OA data are worthless, because OA data give qualitative information about the expected behavior of the pigment in a paint system.

On Stieg's description of the OA paste a procedure is based to calculate from first principles the CPVC of a pigment in a paint system.[11] We know now that the general applicability of this procedure is not justified and only may be applied if Stieg's equation is correct, or if the contribution of the pigment to the total packing of the coating system is small as one sees in many latex coatings.[39,40] The reasonable agreement sometimes found for the calculated and the experimental CPVC is based on the closed loop type of calculation in which the adsorbed layer thickness is the adjustable parameter and also because the presence of aggregates work for the CPVC and the OA value in the same direction. Further, the agreement is not general as earlier work has demonstrated.[37]

For reliably determining CPVC's, the method of Asbeck, et al.[20] is prefered to calculating CPVC's from OA values because the Asbeck method reflects the actual paint much better than the OA paste does.

The presence of aggregated pigment particles also has implications for dispersing powders, certainly for magnetic powders.

To the three well-known stages of the dispersion process: (1) initial wetting; (2) size reduction of the pigment aggregates; and (3) stabilization of the dispersed particles by adsorption; one has to add a fourth process; densification of the aggregated particles.

An illustration of this process can be found in *Table* 4, where one sees a linearly increasing aggregate density, d_{agg}^{OA}, with the logarithm of mixing time. With this result, increasing aggregate density and, therefore, decreasing PVC with mixing time, in combination with wettability effects, the very extensive investigations of Davidson[14] and Wirsching, et al.[31] can now be fully interpreted.

CONCLUSIONS

(1) A description of pigment volume concentration based on average effective particle density is given. The description can be applied to coatings, to dispersions, to powder packings and to oil absorptions. With this model the "aggregates," if present, are taken into account quantitatively.

(2) The different OA values found in practice between different operators and different measuring methods can simply be explained by this "effective particle density" model.

(3) Adsorption of oil onto the pigment surface has, in the cases investigated by us, hardly any effect on pigment packings. For fine, single particles where adsorption can be important, the forces that hold the aggregated particles together are strong compared to the shear forces in the dispersion process. Consequently, the aggregated particle remains relatively large. For coarse single particles the contribution of the adsorbed layer is not important.

(4) The generally accepted description for the OA paste, e.g., as formulated on a volume basis by Stieg,[25] must be considered an extreme case of our model. Unfortunately, the conditions that lead to the Stieg formula are not often met (fulfilled).

(5) Our findings almost completely confirm the theoretical explanation of oil absorption given by Klumpp[42] in 1927.

(6) There is compelling evidence that the model based on the effective particle density gives the right description of a magnetic pigment packing. For non-magnetic pigments the experimental evidence is limited, though the results with the non-magnetic pigments strongly indicates the same mechanism. However, more experiments are needed to establish the general applicability of this model.

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PLASTICS
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COATINGS

Respirator Cartridge Evaluations For Paints Containing Isocyanates

Julia F. Vasta
E.I. DuPont de Nemours & Company, Incorporated*

Organic vapor respirator cartridges have been evaluated for use with Imron® and Centari®, under *conditions which approximate field conditions.* These enamels will henceforth be referred to as Enamel A and Enamel B, respectively. Enamel A is a urethane coating, Type V, according to the ASTM designation, which contains traces of hexamethylene diisocyanate and a mixture of solvents, primarily ethyl acetate and Cellosolve® acetate. Enamel B is a modified acrylic coating, which contains traces of hexamethylene diisocyanate and a mixture of xylenes, toluene, and a variety of other solvents. Although solvent breakthrough was observed under some conditions, isocyanate breakthrough was not observed in any test. During four-hour exposures to Enamel A, neither solvent nor isocyanate breakthrough was observed with the Willson Products R21 organic vapor cartridge. On exposure of this cartridge to Enamel B, acetone breakthrough, followed by other solvents, was observed after 10 hours, but, even after 25 hours, isocyanate breakthrough was not observed. The prefilters used in these studies, R15 and R16, were interchangeable. Ethyl acetate broke through the Mine Safety Appliances organic vapor cartridge (part number 459315) and prefilter (part number 448842) after 15 hours, but isocyanate had not broken through even after 18 hours of exposure to Enamel A. Since ethyl acetate has an odor threshold of 50% recognition of approximately 13 ppm, it can serve as an indicator of the effective end of the cartridge life.

INTRODUCTION

NIOSH has not approved charcoal cartridge respirators for use with isocyanates in the workplace because isocyanates lack warning properties.[1] According to 30 CFR Part 11, the use of respirator cartridges is limited to those gases and vapors whose properties provide the user with some indication that the effectiveness of the sorbant is exhausted and protection is at an end.[2] This study was undertaken to determine that, when used with Imron® and Centari®, henceforth referred to as Enamel A and Enamel B, respectively, organic vapor cartridges are effective in removing solvents and isocyanates from the air and to see whether solvent breakthrough precedes isocyanate breakthrough, thus providing adequate warning of incipient loss of respirator cartridge effectiveness.

A mini paint shop, complete with spray gun, spray booth, and sampling equipment, was assembled in a laboratory hood. Each cartridge was exposed to the enamel atmosphere with a flow rate of 32 L/min at ambient temperature, pressure, and relative humidity. Both the upstream (airborne) and downstream (breathing) air were monitored for solvents and isocyanates during exposure. Solvents were analyzed by direct injection of an air sample into a gas chromatograph; isocyanate was analyzed by drawing a known air volume through a series of midget impingers containing *p*-nitrobenzyl-N-*n*-propylamine and analyzing the resulting urea by liquid chromatography.[3]

Because of the lack of information on the possible effects of different solvents and isocyanates on the adsorption properties of charcoal, these results should not be extrapolated to enamels that differ greatly in solvent and/or isocyanate composition from the enamels tested in this study.

EXPERIMENTAL

Hexamethylene diisocyanate (HDI), *p*-nitrobenzyl-N-*n*-propylamine hydrochloride and distilled-in-glass acetonitrile were obtained from commercial sources. All other reagents used were ACS reagent grade or better and were obtained from various laboratory supply houses.

Enamel A was prepared by mixing three parts of enamel with one part of activator. Its activator contains approximately 5% ether ester (Cellosolve® acetate), 56%

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*Central Research & Development, Experimental Station, Wilmington, DE 19898.
Imron and Centari are tradenames of E.I. DuPont de Nemours & Co., Inc.
Cellosolve is a registered tradename of Union Carbide Corp.

aliphatic ester (ethyl acetate), 5% xylene, and 33% of a polyaliphatic isocyanate derived from hexamethylene diisocyanate. Prior to addition of the activator, Enamel A contains 28% ether ester, 18% aliphatic ester, and 3% aliphatic petroleum distillate. Enamel B was prepared by addition of one gallon of enamel to one pint of activator and mixed with two parts color to one part reducer before spraying. Enamel B activator has approximately the same composition as Enamel A activator. Prior to addition of the activator, Enamel B contains 1% aliphatic ester, 4% aliphatic ketone, 11% toluene, 9% aliphatic petroleum distillate, 20% xylene, and 5% aromatic petroleum distillate. Neither enamel was allowed to age for more than one hour before use.

DESIGN

A schematic of the apparatus used to perform enamel spray tests is shown in *Figure* 1.

A Binks Model 15 spray gun, with a #78 fluid nozzle and a #78S air nozzle, maintained at 40 psi, was used to spray the enamel. To insure a constant flow rate of 32 L/min, a dry test meter, placed in line with the respirator cartridge, was monitored throughout the experiment. NIOSH recommends this flow rate as a simulation of a person with a heavy breathing rate.[4]

Since the prefilter tended to clog with enamel, the pressure drop across the respirator cartridge was monitored throughout each exposure. A maximum pressure drop of 3 in. of water was set, after which the prefilter was discarded. Prefilters were discarded daily, regardless of the pressure drop.

An open Plexiglas® box (34″ × 42″ × 38″) was used to contain the enamel spray. The box was vented by the hood stack which aided in preventing a heavy build-up of the enamel particles.

A total distance of 32 in. was utilized between the cartridge and baffle to create the proper spray conditions. The spray gun was located 24 in. from, but perpendicular to, the wall of the hood, which acted as a baffle to create enamel overspray. The cartridge was placed 8 in. behind the spray gun. This simulated a worker holding the spray gun directly in front of himself at ½ arms' length, spraying a flat object two feet away. The particulate level was maintained at approximately 100 mg/m^3 with these conditions. This particulate level, the maximum observed during actual spray painting at a bodyshop, was used in all subsequent exposures.

The temperature, barometric pressure, and relative humidity were recorded prior to exposure (*Table* 1). Flow rates were adjusted to maintain a flow of 32 L/min. through the respirator and 1.5 L/min. through the upstream and downstream impinger trains.

One additional apparatus modification was incorporated during the Enamel B exposure. Since this enamel contained a variety of solvents, a charcoal tube sampling port was installed directly behind the respirator cartridge. These samples were analyzed by GC/MS to identify the solvents observed breaking through. These included acetone, methyl ethyl ketone, and toluene.

COLLECTION AND ANALYSIS

Isocyanate Samples

A series of three jet impactor type midget impingers, placed both upstream and downstream from the respirator, was used for isocyanate analysis. Unless the impinger and its insert were carefully matched, up to 40% of the isocyanate was found in the second and third impinger. When the tip of the jet of the insert had a diameter not greater than 1 mm and rested no more than 0.5 cm from the bottom of the impinger, no isocyanate was detected in the second or third impingers.

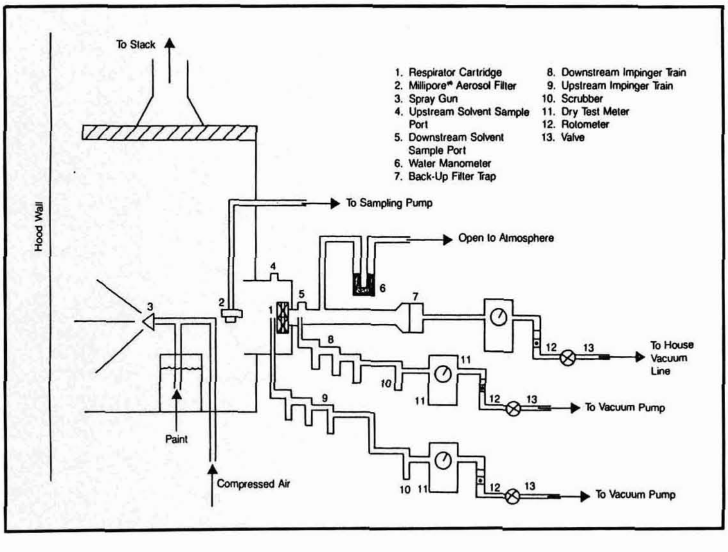

Figure 1—Respirator cartridge exposure chamber and sampling equipment

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Plexiglas is a registered tradename of Rohm and Haas Co.

Table 1—Background Information on Enamel A Exposures

Exposure Number	Cartridge/ Prefilter	Particulate[a] Weight (mg/m³)	Pressure (mm Hg)	Temp (°C)	Relative Humidity (%)	Paint Consumption (g/minute)	Length of Exposure (hours)
1	Willson R 21/R 15	53-120	761	25	61	55	4
2	R 21/R 15	33-142	762	25	50	53	3
3	R 21/R 15	40-320	776	20	26	55	4
4	R 21/R 15	27-133	765	22	53	57	4
5	MSA 459315/448842	27-53	760	23	32	60	4
6	459315/448842	40-53	761	23	34	53	5
7 Day 1	459315/448842	42-93	766	21	39	47	4
Day 2		67-74	766	22	42	53	4
Day 3		44-53	765	22	44	56	4
Day 4		53-93	763	22	36	62	4
Day 5		27-67	760	22	42	53	4

(a) Average of three measurements taken periodically throughout the exposure.

Samples were decanted from each impinger into glass test tubes and evaporated to near dryness, under nitrogen purge, in a water bath at 55°C. Each sample was reconstituted with 3 mL of acetonitrile before analysis on a Hewlett-Packard 1084B liquid chromatograph equipped with a variable wavelength detector.

The analysis of HDI is described by Sango.[3] The method involves HPLC of the derivatized isocyanate with 75% acetonitrile and 25% water containing 1% triethylamine adjusted to pH 3 with phosphoric acid. A 25 cm × 4.6 mm I.D. Du Pont Zorbax® ODS column was chosen for the analysis and the eluted peaks were detected at 254 nm. A 20 μL aliquot of the sample was injected onto the column from the total sample volume of 3 mL. The minimum detection limit was 2 ppb HDI in air.

Since enamel contamination in the upstream impinger was a problem, these samples were centrifuged at 15,000 rpm for 20 min and the supernatant decanted for analysis. To investigate the possibility of losses of HDI from such procedures, aerosolized pigment, without the activator present, was collected, dosed with known quantities of HDI, centrifuged and analyzed, using the same conditions as actual air samples. The recovery of the HDI was 100%. No enamel was ever observed in any downstream sample.

Solvent Samples

Solvent samples for Enamel A were collected by pulling a 1 mL air sample into a gastight syringe and directly injecting it into a Varian Aerograph 600D gas chromatograph equipped with a flame ionization detector. Separation was achieved on a 10′ × ⅛″ stainless steel column containing 10% SE30 on 80/100 mesh Supelcoport kept at 200°C. Samples were collected approximately every 5 min upstream and every 15 min downstream. When breakthrough occurred, the downstream sampling rate was increased.

Separation of the Enamel B solvents was achieved by direct injection of a 1 mL air sample through a gas sampling valve into Hewlett-Packard 5880A gas chromato-

Table 2—Solvent Concentration (ppm) of Enamel A Exposures

Exposure Number	Upstream[a]		Downstream[a]	
	Ethyl Acetate	Cellosolve® Acetate	Ethyl Acetate	Cellosolve® Acetate
1	<2->100	<2->100	ND[b]	ND[b]
2	<2->100	<2->100	ND	ND
3	4->100	<2->100	ND	ND
4	4->100	14->100	ND	ND
5	2->100	5->100	ND	ND
6	<2- 89	2- 49	ND	ND
7 Day 1	3- 97	2- 89	ND	ND
Day 2	4- 117	3- 165	ND	ND
Day 3	<2- 160	<2- 100	ND	ND
Day 4	<2- 66	3- 37	ND	ND
Day 5	<2->100	<2->150	3-17	ND

(a) Concentrations based on an average of approximately 40 air samples taken throughout the exposure.
(b) None detected—minimum detection limit of 2 ppm of solvent.

Table 3—Isocyanate Concentration (ppb) of Enamel A Exposures

Exposure Number	Upstream Elapsed Time[a]					Downstream Elapsed Time[a]				
	1	2	3	4	5	1	2	3	4	5
1	19.8	7.1	17.3	15.0		ND[b]	ND	ND	ND	
2	7.9	22.3	>6.3[c]			ND	ND	ND		
3	40.9	38.5	57.5	43.6		ND	ND	1.6[d]	ND	
4	25.7	22.3	15.6	27.7		ND	ND	ND	ND	
5	7.2	31.7	33.6	30.7		ND	ND	ND	ND	
6	4.3	13.7	7.5	13.7	19.4	ND	ND	ND	ND	ND
7 Day 1	38.4	17.7	49.8	28.6		ND	ND	ND	ND	
Day 2	14.2	20.0	32.4	18.7		ND	ND	ND	ND	
Day 3	20.4	19.7	13.6	10.5		ND	ND	ND	ND	
Day 4	10.3	4.0	15.2[e]			ND	ND	ND[e]		
Day 5	8.0	9.7	15.3	16.3		ND	ND	ND	ND	

(a) Hours into the exposure; samples collected every hour.
(b) None detected—minimum detection limit of 1 ppb.
(c) One impinger spilled.
(d) Possible contamination of the sample.
(e) Actual sampling time 45 minutes.

graph equipped with a flame ionization detector. Separation was achieved on a 30 meter fused silica capillary column coated with OV 101. An oven temperature program from 35°C to 225°C in 20 min was used. Solvent sample concentrations in ppm (vol to vol) were determined by comparing peak heights of the sample against a standard curve.

Particulate Samples

Particulates were collected with a Millipore® open faced cassette suspended directly in front of the cartridge during the paint exposure. A 7.5 L air sample was collected on a preweighed 47 mm glass fiber filter. The filter was allowed to dry overnight in a closed container and the weight gain due to the dry paint particles was measured.

RESULTS AND DISCUSSIONS

Enamel A Study

Tables 1, 2, and 3 summarize the background and analytical data for the determinations of HDI and ethyl acetate and Cellosolve acetate in Enamel A at particulate levels of approximately 100 mg/m^3 with the arrangement of apparatus as described in *Figure* 1. Note that particulate levels are by no means a quantitative measurement due to variations in the properties of the mixed enamel as it polymerizes; air currents in the hood; partial clogging of the spray gun; paint droplet diameter, and temperature. Therefore, this measurement can be used only as a guide to approximate the concentration of enamel particles which would be present in the test atmosphere.

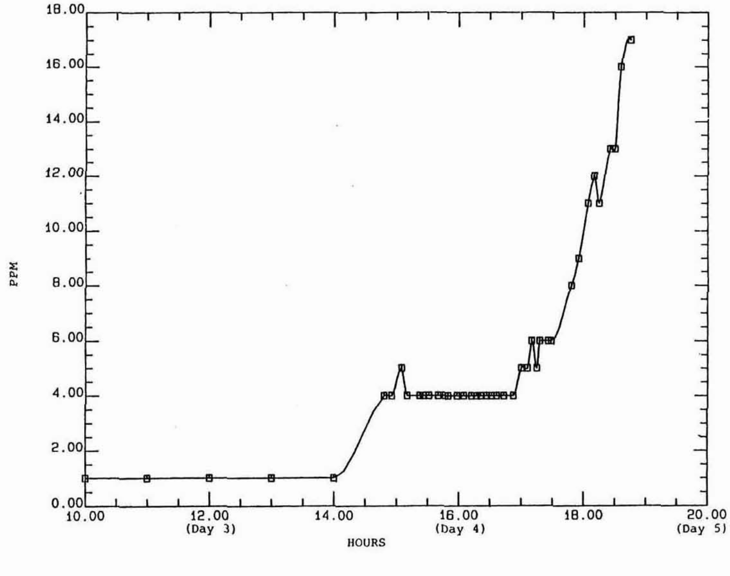


Figure 2—Ethyl acetate breakthrough data (Enamel A)

Table 4—Background Information on Enamel B Exposure (25 Hours)

Exposure Date	Cartridge/ Prefilter	Particulate[a] Weight (mg/m³)	Barometric Pressure (mmHg)	Temp (°C)	Relative Humidity (%)	Paint Consumption (g/minute)	Length of Exposure (hours)	Cartridge Weight Gain (grams)
Day 1	Willson R 21/R 16	85–145	755	22	53	26	5	3.20
Day 2	R 21/R 16	53–89	759	23	45	38	5	1.60
Day 3	R 21/R 16	107–174	760	22	43	28	5	4.00
Day 4	R 21/R 16	93–213	757	22	45	29	5	3.79
Day 5	R 21/R 16	133–200	759	22	—[b]	34	5	2.74

(a) Based on an average of three measurements.
(b) Measurement not taken.

Table 5—Solvent Concentration (ppm) of Enamel B Exposure (25 Hours)

	Upstream				Downstream			
Exposure Date	Acetone	Methyl Ethyl Ketone	Ethyl Acetate[a]	Toluene[a]	Acetone	Methyl Ethyl Ketone	Ethyl Acetate	Toluene
Day 1	<2-8	2-9	—	—	ND[b]	ND[b]	ND[b]	ND[b]
Day 2	<2-6	<2-8	—	—	ND	ND	ND	ND
Day 3	5-12	7-11	—	—	<2-15	ND	ND	ND
Day 4	<2-5	<2-7	—	—	<2-15	<2-4	ND	ND
Day 5	6-47	<2-22	<2-9	7->100	12-70	13-105[c]	<2-16	<2->100

(a) Not measured until breakthrough of solvent occurred.
(b) None detected with a minimum detection limit of 2 ppm solvent.
(c) Due to the effects of storing the exposed cartridge overnight; see Figure 2.

Table 6—Isocyanate Concentration (ppb) of Enamel B Exposure (25 Hours)

Exposure Date	Upstream Elapsed Time[a]					Downstream Elapsed Time[a]				
	1	2	3	4	5	1	2	3	4	5
Day 1	8.1	3.9	7.4	8.9	3.7	ND[b]	ND	ND	ND	ND
Day 2	5.3	6.2	2.7	4.9	3.7	ND	ND	ND	ND	ND
Day 3	5.3	5.9	6.2	10.2	8.1	ND	ND	ND	ND	ND
Day 4	6.2	4.3	6.4	6.5	7.1	ND	ND	ND	ND	ND
Day 5	5.8	5.1	2.4	8.3	5.9	ND	ND	ND	ND	ND

(a) Hours into the exposure; samples collected every hour.
(b) None detected with a minimum detection limit of .5 ppb HDI.

Short duration breakthrough studies (four hours) were performed with the Willson Products' R21 organic vapor cartridge in conjunction with the R15 prefilter. The prefilter consisted of ½ in. thick fiberglas backed with a fiber pad. Neither isocyanate or solvents broke through the Willson cartridge after four hours. (Willson Safety Products is located in Reading, PA)

Long duration breakthrough studies (20 hours) were performed with Mine Safety Appliances' (MSA) organic vapor cartridge (part number 459315) and prefilter (part number 448842). No isocyanate broke through the MSA cartridge after 18.75 hours. The cartridge was evaluated for four hours on each of five consecutive days. It was stored overnight wrapped in aluminum foil and sealed in a plastic bag to prevent the charcoal from equilibrating with the atmosphere. At the fifteenth hour, ethyl acetate was observed at approximately 6 ppm in the downstream (breathing) air (*Figure* 2).

Enamel B Study

Tables 4, 5, and 6 summarize the background and analytical data for the determinations of HDI, acetone, methyl ethyl ketone, ethyl acetate, and toluene that were measured during a 25-hour exposure, using the Willson Products' R21 organic vapor cartridge with R16 prefilter. The prefilter consisted of a polyethylene pad backed by a fiber pad. (Both the R15 and R16 are rated for use with

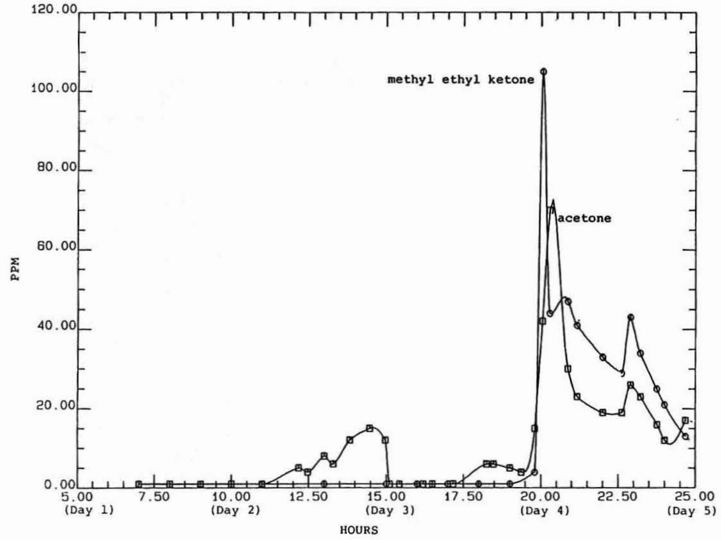


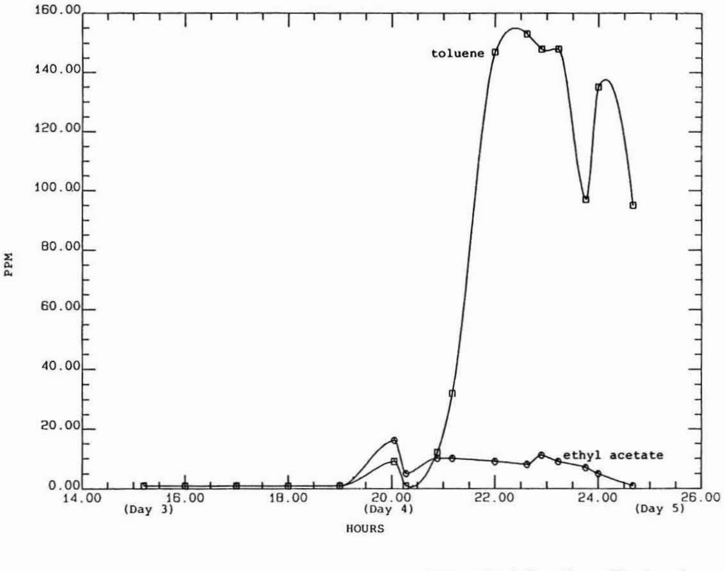
Figure 3—Acetone and methyl ethyl ketone breakthrough data (Enamel B)

paint and enamel mists so, for purposes of this study can be considered as interchangeable. The R15 is also rated for use with pesticides, but the R16 is not.) The apparatus was identical to the one used for the Enamel A study.

After 25 hours, no isocyanate had broken through the cartridge. The cartridge was evaluated for five hours on each of five consecutive days. Protection of the cartridge from the atmosphere was the same as in the Enamel A study. At the tenth hour, acetone was observed in the downstream (breathing) air, followed by methyl ethyl ketone at the twentieth and ethyl acetate and toluene at the twenty-first hour of exposure (*Figures* 3–4). Smaller molecules, such as these, will break through the cartridge first, i.e., acetone, methyl ethyl ketone, and ethyl acetate, followed by the bulkier aromatics, e.g., toluene. Toluene has the lowest odor threshold at 50% recognition (2 ppm) of all these solvents.[5] However, before toleune can be detected, a worker may be exposed to low levels of acetone, methyl ethyl ketone, and ethyl acetate for a significant period of time (*Table* 5). Although the breakthrough time for ethyl acetate in the study was somewhat longer than in the Enamel A study (21 hours vs 15 hours), in each case, breakthrough took place at the end of the fourth day of exposure.

Figure 3 shows the breakthrough data for methyl ethyl ketone (MEK) and acetone. Note the high level of MEK

Figure 4—Toluene and ethyl acetate data (Enamel B)



observed during the first few minutes of the fifth day of exposure. When the cartridge was stored overnight, the solvent absorbed on the charcoal reached equilibrium with the air inside the cartridge and, when air was pulled through the cartridge, a large concentration of solvent vapor appeared downstream. This does not reflect the true downstream concentration at that time.

This same phenomenon can be expected to occur if the worker reuses the cartridge after prolonged storage. A worker may be briefly exposed, without warning, to solvent vapors when the cartridge is first used.

CONCLUSIONS

Enamels A and B were sprayed from a Binks Model 15 spray gun to form an atmosphere for testing organic vapor respirator cartridge effectiveness against enamel components, primarily hexamethylene diisocyanate (HDI). Both cartridges evaluated were effective against HDI at particulate concentrations which were found in a representative body shop. No HDI breakthrough was observed in any of the tests. Test duration varied from test to test.

In the Enamel A environment, the Willson Products' R21 organic vapor cartridge, with R15 prefilter, provided adequate protection for a minimum of four hours, with no isocyanate or solvent breakthrough detected. The Mine Safety Appliances' (MSA) organic vapor cartridge (part number 459315) with prefilter (part number 448842) provided adequate protection up to 18.75 hours against HDI. During the fifteenth hour of this same exposure, ethyl acetate was detected breaking through the cartridge.

In the Enamel B environment, the Willson Products' R21 organic vapor cartridge, with R16 prefilter, provided adequate protection up to 25 hours against HDI. During this same study, acetone broke through the cartridge at the tenth hour, followed by methyl ethyl ketone, ethyl acetate, and toluene.

Because of the lack of information on the possible effects of different solvents and isocyanates on the adsorption properties of charcoal, these results should not be extrapolated to enamels that differ greatly in solvent and/or isocyanate composition from the enamels tested in this study.

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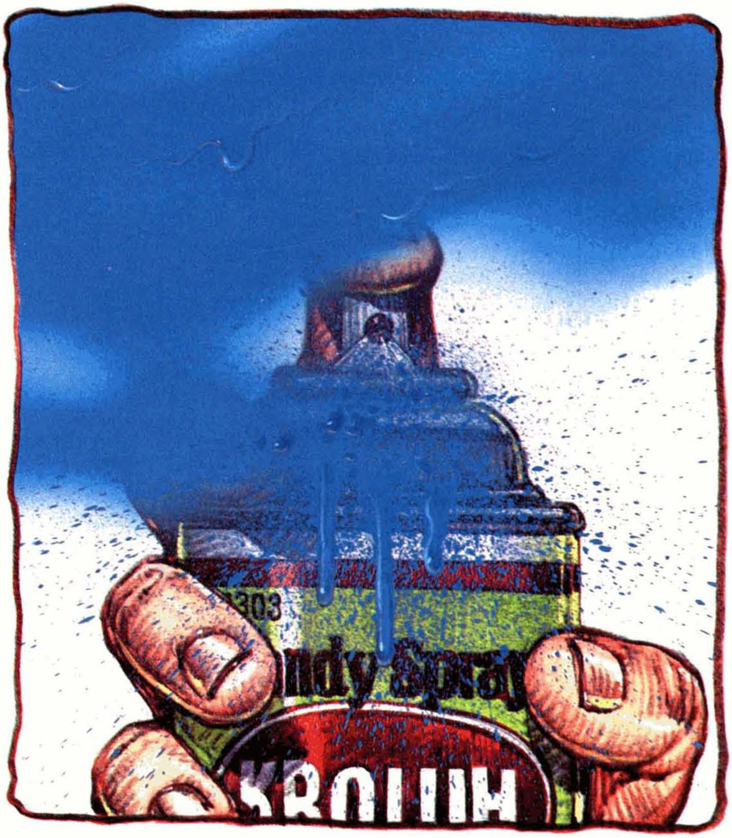

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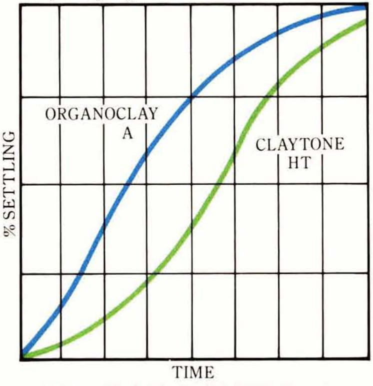

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Determination of Pentachlorophenol Acrylate Purity by High Performance Liquid Chromatography

Darryl A. Frick
PPG Industries, Incorporated*

A method for the separation and quantification of pentachlorophenol acrylate, a fungicidal monomer, has been developed. The method uses non-aqueous reversed phase high performance liquid chromatography (HPLC). The chromatography was accomplished using a mobile phase of 9/1 methanol/tetrahydrofuran (V/V), a C18 column, and ultraviolet detection at 254 nm. The separation was complete in less than five minutes.

An estimate of the amount of free pentachlorophenol was also obtained using this method.

Introduction

Recently, there has been interest in incorporating paint fungicides into polymer backbones to overcome the problem of fungicidal volatility and solubility.[1,2] One of the fungicidal monomers studied was pentachlorophenol acrylate (PCPA). PCPA can be prepared from acryloyl chloride and pentachlorophenol.[1]

As further work in the use of PCPA is anticipated, a method to easily assay the purity of prepared PCPA was needed. Additionally, the concentration of pentachlorophenol (PCP) that did not react during the preparation of PCPA is of interest as PCP has been shown to be toxic to humans[3] and a technique to estimate the amount of free PCP was also required.

The literature has references to the determination of PCP using high performance liquid chromatography (HPLC) in both the normal phase[4] and reversed phase[5] modes. It was decided that PCPA and PCP would most easily be separated and quantified using a reversed phase HPLC separation as PCPA has considerable non-polar character.

Experimental

EQUIPMENT: The chromatograph consisted of a M6000A pump, U6K injector, and 440 absorbance detector (Waters Associates, Milford, MA). The columns used were either a Brownlee LiChrosorb RP-18 (Rainin Instrument Co., Woburn, MA) or a Whatman Partisil 5/25 ODS (Alltech Associates, Kennett Square, PA). Both columns had the dimensions 4.6 mm × 250 mm. Chromatographic peaks were recorded on a model 3380A integrator (Hewlett-Packard, Avondale, PA).

MATERIALS: HPLC grade methanol and tetrahydrofuran (Fisher Scientific Co., Pittsburgh, PA) were used without further purification. Pentachlorophenol was obtained from Supelco, Inc. (Bellefonte, PA) and was used without further purification. Pentachlorophenol acrylate was prepared by Polysciences (Warrington, PA). This crude monomer had a melting point range of 78-80°C. A portion of the PCPA was recrystalized from ethyl ether until a constant melting point was obtained (82.5°C). This purified PCPA was used as a standard. The presence of PCPA was confirmed by ^{13}C NMR.

CHROMATOGRAPHIC CONDITIONS: The mobile phase was 9/1 methanol/tetrahydrofuran (volume/volume) and the flow rate was 1.5 mL/min. Samples were dissolved in tetrahydrofuran prior to injection. The injection volume was 5 μL. Peaks were detected by ultraviolet absorbance at 254 nm.

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*Coatings & Resins Div., P.O. Box 9, Allison Park, PA 15101.

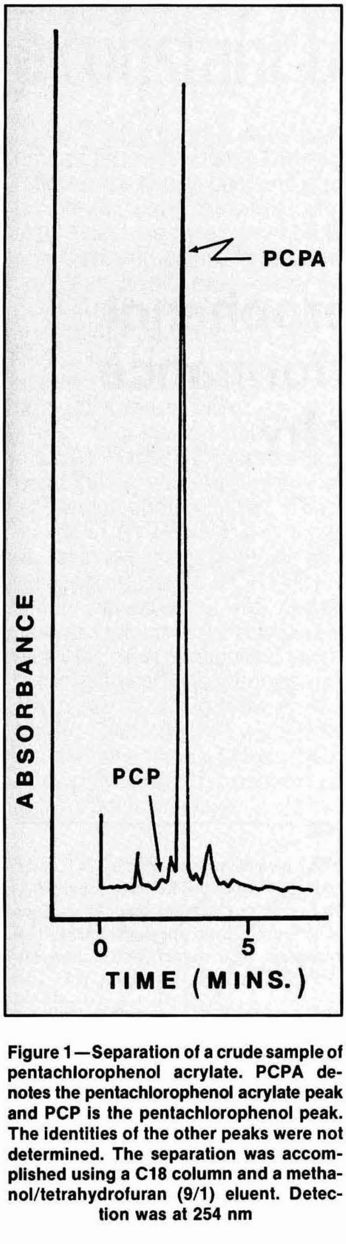

Figure 1—Separation of a crude sample of pentachlorophenol acrylate. PCPA denotes the pentachlorophenol acrylate peak and PCP is the pentachlorophenol peak. The identities of the other peaks were not determined. The separation was accomplished using a C18 column and a methanol/tetrahydrofuran (9/1) eluent. Detection was at 254 nm

DARRYL A. FRICK received a BA Degree from St. Cloud State University and a MS Degree from North Dakota State University. Since joining PPG Industries, Coatings and Resins Div., he has been a specialist in high performance liquid chromatography for the separations group of the analytical department.

He is a member of the Society for Analytical Chemists of Pittsburgh and a member of the American Chemical Society. He has authored or co-authored several papers dealing with analytical problems.

Results and Discussion

Initial work on the separation of PCPA utilized traditional aqueous-organic reversed phase separation with methanol as the organic component. It was found that even with a mobile phase of only methanol, the time necessary to elute PCPA was too long.

Parris[6] has noted that by employing a mobile phase composed of two organic solvents, low polarity compounds could be determined in less time than was necessary for a separation using an aqueous-organic mobile phase. Furthermore, selectivity is not necessarily sacrificed using non-aqueous reversed phase separations. The principle of developing a separation using a mixture of a more polar solvent and a less polar solvent for a mobile phase applies to non-aqueous reversed phase as well as traditional reversed phase separations.

For the determination of PCPA and PCP, the more polar solvent was methanol and the less polar solvent was tetrahydrofuran. A mixture of one part tetrahydrofuran and nine parts methanol (volume/volume) was found to elute the compounds of interest in less than five minutes (*Figure* 1).

No primary standard of PCPA was available so the crude PCPA sample was determined versus a sample of the crude monomer which had been recrystalized until a sharp melting point had been obtained. Using the described HPLC method, the crude monomer was determined to contain 95.1% PCPA. Additionally, the purity of the sample was determined using an equivalent weight based on the degree of unsaturation.[7] The equivalent weight determined indicated a concentration of PCPA in the crude monomer of no higher than 97%, assuming the only impurity is acryloyl chloride.

While the separation was not optimized for the determination of PCP, an estimate of the concentration of PCP was also obtained using the method outlined. The total free PCP was found to be 0.58%. Although this result was not confirmed by an independent technique, the amount of PCP found indicates one should take the proper precautions when handling crude PCPA monomer. Both PCPA and PCP were determined versus external standards.

Summary

The amount of pentachlorophenol acrylate in a crude monomer sample has been determined using high performance liquid chromatography. The non-aqueous reversed phase separation took less than five minutes. The accuracy of the method was tested versus an equivalent weight method with the results of the two methods differing by only 2%.

An estimate of pentachlorophenol was also obtained using the high performance liquid chromatographic method.

Acknowledgments

I wish to thank Dr. Joseph Benga for his work in purifying the crude PCPA, Mr. Timothy Sanford for the ^{13}NMR work, and Mr. John Shutak for the equivalent weight determinations.

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Society Meetings

BALTIMORE .... FEB.

"Leveling and Surface Flow in Coatings"

"LEVELING AND SURFACE FLOW IN COATINGS AND THEIR RELATIONSHIP TO SURFACE PHENOMENA" was presented by Wolfgang Zinnert, of Byk-Mallinckrodt.

Mr. Zinnert briefly reviewed the history of flow and leveling of coatings as found in literature and stated that problems are more severe in modern coatings. After defining flow and leveling, he described factors which affect them, including wet film thickness, viscosity, dry time, and surface tension. According to Mr. Zinnert, agents used to improve flow and leveling include solvents, linear resins and linear silicones. Linear resins, such as CAB and polyacrylates, are primarily used in industrial coatings.

Using a slide demonstration, Mr. Zinnert showed that CAB, silicones, and polyacrylates are actually anti-flow agents because incompatibility of the additive on the surface of the film affects flow. After defining surface tension, he stated that a liquid will wet a surface which has a surface tension equal to or less than the liquid. Slides giving the surface tension of various solvents, coatings and surfaces, and the methods of measuring these, were shown. In addition, Mr. Zinnert demonstrated the effects of additives on surface tension measurements and how these translate into better flow and leveling. The larger the area under the surface tension plot, the better the flow, he said.

According to Mr. Zinnert, CAB, silicones, and polyacrylates are surface flow additives and not flow and leveling additives. In conclusion, he reviewed the contributions of these additives to a coating film and reviewed some of the problems they can cause, such as cratering, hydrolizing, and recoat problems.

Dr. Gene Holman, of Essex Community College, spoke on "MOTIVATION AND PRODUCTIVITY."

According to Dr. Holman, motivation entails discovering an employee's need and realizing that need. He discussed a hierarchy of these needs, including physical, security, social, esteem, and self-actualization needs. Dr. Holman concluded with a description of theories used by companies to motivate their employees, while revealing that there is no easy formula which will guarantee success.

FRANK GERHARDT, *Secretary*

BIRMINGHAM .... FEB.

"Monitoring Lead in Paint Production"

Mr. A.C.D. Cowley, of I.C.I., spoke on "MONITORING LEAD IN PAINT PRODUCTION."

Mr. Cowley stated that lead has a measurable effect on health at lower levels than previously considered safe. Under the provisions of "The Control of Lead at Work Regulations, 1980," employers must determine both the nature and degree of exposure.

Emphasizing the importance of correct sampling of lead levels in the air, Mr. Cowley described the sampling methods used by I.C.I. He gave the results of investigations performed in a variety of departments at different paint factories. Although the findings traced significant levels in some areas over a short sampling time, the eight hour time weighted averages were very low, he said. Mr. Cowley concluded that, while regulations involved a great deal of work, the results showed no evidence of significant risk.

DON CLEMENT, *Secretary*

CLEVELAND .... FEB.

"Aqueous and Nonaqueous Latex Dispersions"

"STABILIZATION TECHNIQUES OF AQUEOUS AND NONAQUEOUS LATEX DISPERSIONS" was presented by I. Krieger, a Professor at Case Western Reserve Univ. and Director of the Case Center for Adhesives, Sealants, and Coatings.

Dr. Krieger emphasized the importance of steric stabilization. He then used dimensionless group analysis to correlate rheology with stabilization morphology in latex systems.

SCOTT RICKERT, *Secretary*

DETROIT .... JAN.

"Computer Color Control"

Norman Uress, of Applied Color Systems, Inc., spoke on "COMPUTER COLOR CONTROL."

Mr. Uress' presentation focused on the Visual Color System (VCS) device. He stated that, while the basic concept of the VCS is derived from the spinning disk developed by J.C. Maxwell in the mid-nineteenth century, the system employs modern microprocessors and instrumentation technology to achieve precise control, high accuracy, and repeatability. The VCS can be a useful tool to the color stylist as well as being used as a quality control device, he stated.

Q. How many colors does it take to match a standard?

A. The color that is seen on the VCS is only a visual sensation. When the VCS is used in conjunction with an ACS computer color system, it is then possible for the formulator to decide how many pigments he wants to use to match any given color standard. The computer will then pick the pigments (from library of pigments) to give the best possible match.

ALLAN Q. MOY, *Secretary*

LOUISVILLE .... FEB.

"Acid Catalysis of Coatings"

Symposium Chairman Joyce Specht, distributed a checklist for employers entitled "Early Steps to Compliance" to be used as a reference guide in preparation for compliance to Federal OSHA "Right to Know" regulation.

Don Collier, Chairman of the Technical Committee, apprised members of the FSCT proficiency testing for laboratories in their test procedures and in standardization of equipment.

Dr. Len Calbo, Vice-President of Marketing for King Industries, spoke on "ACID CATALYSIS OF COATINGS."

Dr. Calbo emphasized high solids. He discussed the reaction of acid catalysis with amino and polyester systems.

M. JOYCE SPECHT, *Secretary*

NORTHWESTERN .... FEB.

"Federation Officers Visit"

Honored guests in attendance were Terryl F. Johnson, Federation President, and Frank Borrelle, Executive Vice-President. Mr. Johnson reported on the Montreal Annual Meeting and discussed the 1984 Annual Meeting in Chicago.

Mr. Borrelle detailed the changes involved with the PRI. Additional topics discussed included the financial position of the Federation, future expansion plans, and the planning of future joint meetings between the Federation and NPCA. Mr. Borrelle spoke about the growing national and international membership and the officers/staff meeting in Louisville in May. He requested that Constituent Societies participate in helping to restore the Boston Paint Store.

ALFRED F. YOKUBONIS, *Secretary*

PACIFIC NORTHWEST ... JAN.
Vancouver (B.C.) Section

"Emulsions"

Patrick J. McDonald, of Reichhold Chemicals Inc., spoke on "A PRACTICAL APPROACH TO UNDERSTANDING EMULSIONS."

After a comparative description of latexes versus emulsions, Mr. McDonald discussed the actual processing procedures of emulsions. He stated that the basic ingredients are water, monomer, surfactants, initiator or catalyst, protective colloid, and pH buffers. After describing the equipment used and the actual kettles in production, he listed the processing variables which affect the physical properties of the emulsion. Mr. McDonald concluded with an analysis of particle size and molecular weight as two important factors that determine latex paint properties.

YVON POITRAS, *Secretary*

PITTSBURGH .... MAR.

"Trends and Future Coatings"

Clifford Schoff, Society President-Elect, was presented with the Trigg Award for 1984, in recognition for his outstanding service as Society Secretary in 1982–83.

Initiating their new monthly feature, "The Computer Corner," the Technical Committee covered three articles in various trade journals. Topics included the use of computers to design latex flat paints, the use of computers in marketing coatings, and tax incentives for computerization.

Society President, Michael Gillen, reported on the efforts of the Education Committee to provide speakers from the Society to the greater Pittsburgh area public school system. An outline, entitled "Mechanisms of Film Coatings," will serve as a basis for such presentations, he said.

Dr. Marco Wismer, of PPG Industries, Inc., presented "TRENDS AND FUTURE COATINGS."

According to Dr. Wismer, the value that all coatings provide cannot be underestimated. While there are great potentials for the coatings industry today, growth has not been as dramatic as it should be, he stated. He believes that too many companies have sacrificed quality to make short term sales. Dr. Wismer touched upon some strategic goals which will help improve the image of the coatings industry. These include: increased corrosion protection, the elimination of solvents, conservation of energy, the reduction of toxic hazard potential and waste hazard potential, cost reductions while maintaining product quality, and improvement of coatings durability and overall performance.

In the area of toxicity, he believes that products should be produced with low toxicity, and that consumers should be made aware of all features of a coating. To eliminate solvents, high solids, waterbased, and powder coatings are being used. Dr. Wismer pointed out, however, that solvents will never be fully eliminated, and that when they are reduced, replacement coatings are not free from problems.

Dr. Wismer stated that, as far as the future is concerned, there are many opportunities open to firms with an imaginative outlook. He discussed opportunities in the areas of corrosion inhibitors and in new cure mechanisms for urethanes and epoxies, higher performing opacifiers, and specialty rheology aids, aimed at high performance resins. He concluded by encouraging firms to look at new concepts in the solving of problems and to expand research efforts to meet these problems.

JOSEPH L. MASCIA, *Secretary*

FSCT Membership Anniversaries

50-YEAR MEMBERS

New York

Joseph Cantor, Josad Consultants, Inc.
Joseph Cataldo, Retired.
Richard O. Innes, O.G. Innes Corp.
Charles H. Levine, Consultant.
Sidney B. Levinson, Retired.
Monroe Rapaport, Pyrolac Corp.
Elias Singer, Troy Chemical Corp.
Herman J. Singer, Retired.

Southern

Michael J. Catena, Chemex Paint & Coatings, Inc.
Carl L. Engelhardt, Consultant.
William Rose, Retired.

25-YEAR MEMBERS

Birmingham

R.W. English, Mastermix Engineering.

New York

Donald E. Brody, Skeist Laboratories, Inc.
Glen W. Danziger, Seaboard Chemical Corp.
Marvin Kress, Red Devil Paints & Chemicals
Thomas Luyster, Jr., John L. Armitage & Co.
Angelo Mangravite, Red Mills Paint & Chemicals.
Norman J. Mechanic, Standard T Chemical Co.
Bernard Newfield, Proco International
Leonard Schaeffer, Leneta Co.
Richard Schmidt, Proctor Paint & Varnish Co.
Alex Siegel, Retired.
F. Albert Smiles, Con-Lux Coatings, Inc.
Saul Spindel, D/L Laboratories.
Robert P. Waterbury, Standard T Chemical Co.
Curtis Young, Mercury Paint Corp.

Pittsburgh

Edward Neuwirth, Watson Standard.

Southern

Harold Krause, Bruning Paint Co.
Ronald L. Sadler, Mobay Chemical Corp.

WESTERN NEW YORK .... FEB.

"Propylene-Based Glycol Ethers"

"PROPYLENE-BASED GLYCOL ETHERS" was presented by Dr. Roger Heckman, of Arco Chemicals.

Dr. Heckman stated that propylene-based glycol ethers and propylene glycol methyl ether acetate offer high performance, low toxicity choices for use in a wide range of coatings applications. Laboratory comparison indicates that performance characteristics of paints formulated with propylene-based products are very similar to performance characteristics of paints currently being formulated with ethylene-based products.

Dr. Heckman discussed studies showing that P-series glycol ethers have a dramatically safer sub-chronic toxicological profile than E-series ethers. He presented a summary of the historical development of the concern over the reproductive toxicity of certain ethylene glycol ethers and acetate derivitives.

CHARLES C. TABBI, *Secretary*

Future Society Meetings

Baltimore

(May 17)—Annual Business Meeting and Election of Officers.
(June)—Joint Outing with BPCA.

Cleveland

(May 21)—Annual Meeting/Spouses' Night. "Paint Examination Techniques Utilized in the FBI Laboratory"—James E. Corby, Federal Bureau of Investigation.

Detroit

(May 15)—Joint Meeting with DPCA.

Golden Gate

(May 16)—"The Proper Software for You"—L.S. Feldman, Sinclair Paint Co.

Kansas City

(June 8-9)—Joint Meeting of the Kansas City and St. Louis Societies.

Los Angeles

(June 13)—Annual Meeting/Election of Officers. Technical Committee Program.

Pacific Northwest

(May 17)—"The Proper Software for You"—L.S. Feldman, Sinclair Paint Co.

Piedmont

(May 16)—"Inerting for Safety in Coatings Plants"—Kevin Donahue, Neutronics, Inc.
(June 20)—"Composite vs. Single Dispersant in Colorants and Coatings"—Elio Cohen, Daniel Products Co.

St. Louis

(May 15)—Manufacturing Night.

Elections

BALTIMORE

Active

Foskey, Gregory S.—Sherwin-Williams Co., Baltimore, MD.

Hansen, Donna L.—Sherwin-Williams Co., Baltimore.

Associate

McNiff, Joseph P.—McWhorter, Inc., Cherry Hill, NJ.

Spitzer, Ronald G.—Cosan Chemical Corp., Carlstadt, NJ.

NEW YORK

Active

Altamirano, Lloyd E.—United Technologies Inmont, Clifton, NJ.

Baird, Edward—Norton and Son, Bayonne, NJ.

Butler, Bob—Penn Jersey Paint Co., Newark, NJ.

Doviak, William C.—Alfa Ink Division, Carlstadt, NJ.

Lazaro, Jr., Mario—DL Laboratories, New York, NY.

Lefkovic, Leslie Z.—American Abrasive Met., Irvington, NJ.

Levinson, Sidney B.—Sidlev Associates, Cranbury, NJ.

Litwin, Gerald J.—Henkel Corp., Hoboken, NJ.

Muldrow, Charles N.—Shamrock Chemical Co., Newark.

Pisapia, John—No. Brunswick Coatings, North Brunswick, NJ.

Rasoilo, Maria-Isabel—Henkel Corp., Hoboken.

Shu, Homer—International Paint Co., Inc., Union, NJ.

Associate

Broadhurst, Geoffrey W.—CIBA-GEIGY Corp., Hawthorne, NY.

Corwith, Charles L.—R&A Specialty Chemical Co., Brooklyn, NY.

Howard, Robert—D.H. Litter Co., New York, NY.

McGlinn, James—Alcan Ingot & Powders, Union, NJ.

Moffat, David—Rohm and Haas Co., Elmwood Park, NJ.

Tygett, W. David—Alcan Ingot & Powders, Union.

SOUTHERN

Active

Bullman, Alan R.—Superior Sealants, Atlanta, GA.

Garver, Clyde M.—Horizon Chemical, Clearwater, FL.

Harvley, David—Ameron Inc., Enmar Finishes Inc., Little Rock, AR.

Hourigan, Robert M.—Dyco Chemicals, Inc., Clearwater.

Krannacker, James B.—Redland Prismo, East Point, GA.

Mayoka, Steven R.—Redland Prismo, East Point.

Rocc, Peter J.—Glidden Coatings, Atlanta.

Sherrill, Reuben—Glidden Coatings, Atlanta.

Vergne, Alvaro F.—Coronado Paint Co., Edgewater, FL.

Villani, David P.—Redland Prismo, East Point.

Weems, James E.—Commercial Coatings Corp., Miami, FL.

Whitney, Grayden D.—Union Chemicals Div., Ft. Lauderdale, FL.

Associate

Armstrong, Deanna Y.—Sylvachem Corp., Roswell, GA.

Bradbury, Doug—Mat Chemical Inc., Hialeah, FL.

Docherty, Paul E.—Eastman Chemical Prod., Inc., Belleair Bluffs, FL.

Edwards, Kathy—Mat Chemicals Inc., Tampa, FL.

Fletcher, Suzanne—Eastman Chemical Prod., Inc., Duluth, GA.

Framil, Carlos—Mat Chemicals Inc., Hialeah.

Gallas, Rick—S.C. Johnson & Son., Charlotte, NC.

Marria, V.J.—Amer Int'l Cont., Inc., Tampa.

McCard, J. Harold—N L Industries, Atlanta, GA.

Nicholson, John B.—Davies Can Co., Atlanta.

Phipps, Susie J.—Standard Container, Tampa.

Reker, Kenneth R.—Harshaw Filtrol, Memphis, TN.

Skinner, L. Gerry—Tioxide America Inc., Melrose, CT.

Tobin, Glenn W.—Amer. Int'l Cont., Inc., Tampa.

Waxmonsky, John S.—Morehouse Industries, Tucker, GA.

Wells, Robert H.—R.H. Wells & Co., Lakeland, FL.

Educator/Student

Boyer, Peter L.—University of Southern Mississippi, Hattiesburg, MS

Santobianco, John G.—Ingalls Shipbuilding, Ocean Springs, MS.

Southern Society Draws Attendance of 447 To 50th Anniversary Meeting in Florida

The largest attendance in its history, 447, was set at the Fiftieth Anniversary Meeting of the Southern Society, March 7-9, at Clearwater Beach, FL.

The Program Committee was chaired by Society Vice-President James E. Geiger, of Sun Coatings, Inc., and his wife, Lynne. Working with them were the other three officers and their wives: President William G. Early, of Piedmont Paint Mfg. Co., and Faith; Secretary Salvatore Sanfilippo, of Reichhold Chemicals, Inc., and Emma; and Treasurer Ronald R. Brown, of Union Chemicals Div., and Irene.

Program Sessions

Highlighting the program sessions was the Keynote Address—"Meeting the Challenge of Managing Change"—by Robert E. Pajor, President and Chief Operating Officer of the Valspar Corp. Mr. Pajor reviewed the past, present, and future of the paint and coatings industry and analyzed the factors, trends, and changes which affect U.S. industry in general, and the paint industry in particular.

Other presentations were:

"The Paint Industry—Then and Now"—by Al Hendry, of A.L. Hendry & Co., and Thomas F. Marek, of Coronado Paint Co.

"Product Liability From an Attorney's Viewpoint"—by Michael Smith, Esq.

"Label Development From the Printer's Viewpoint"—by John M. Barnes, of Southprint Corp.

"Computers and Hands-on Experience"—by representatives from Apple Computer, Inc., Business Software Concepts, Inc., and Information Management Systems, Inc.

"The Future is Spelled With a 'U' for Urethane"—by Edward W. Lewandoski, of Rohm and Haas Co. (Design of a Urethane Coating); and Henry A. Kasprzak, of Spencer-Kellogg Div. (Recent Developments in Urethanes).

The annual Gadgets and Gimmicks competition, chaired by Robert F. Link, of R.T. Vanderbilt Co., drew eight entries this year:

(1) Mud-Cracking Test Procedure
(2) High-Speed Laboratory Mill
(3) An R&D Project Worksheet
(4) Continuous Drum Filling
(5) Single Pigment System of Pigment Evaluation
(6) A System to Minimize Time on Retrieving Resins and Pigments
(7) An Economical and Convenient Structure for Exterior Paint Panel Exposure
(8) Field Test Viscosity Can Tester. This device, by Jack E. Benham and Jules Gachette, of Commercial Coatings Corp., was declared the winner.

All G&G's are expected to be published later this year in the JCT.

Awards Luncheon

The feature attraction at this annual event was the presentation of 50-year membership pins and pens (with the compliments of the Federation) to:

Michael J. Catena, who entered the paint industry in 1928 with the Larkin Co., in Buffalo, N.Y. He later joined the McDougall-Butler Co. In 1946, Mr. Catena moved to Tampa where he co-founded Harris Paint Co. The company was sold to Grow Chemical and he remained with Grow as Regional Vice-President and President of five Grow companies until he retired from Grow in 1971. Since then, Mr. Catena has operated Chemex Paint and Coatings, Inc. He is a Past-President of the Western New York and Southern Societies and the Florida PCA.

Carl L. Engelhardt, who joined Brooklyn Paint & Varnish Co. in 1931 and stayed with them for 32 years. He moved to Florida in 1963 where he has since operated a consulting and test fence business. Mr. Engelhardt is a Past-President of the New York Society.

William Rose, whose paint industry career began with the Ernie Calman Co. in 1927. He was associated with several paint manufacturers for 35 years, mostly in the south. From 1962-69, he worked for the Georgia Institute of Technology.

Twenty-five year membership pins were presented to: Harold Krause, of Bruning Paint Co.; Ronald L. Sadler, of Mobay Chemical Co.; Bud Rystrom; and Bob Willard.

Terryl Johnson, Federation President, congratulated the Society on its golden anniversary and presented President Early the traditional anniversary attache case and congratulatory scroll.

A $750 contribution from the Southern Society to the Paint Research Institute was presented by President Early to Frank J. Borrelle, Federation Executive Vice-President.

The luncheon speaker was Noris L. Johnson, of the Warren Rupp Co., who gave a motivational talk on "All Three You's."

New Officers

The slate of officers elected for 1984-85 are: *President*—James E. Geiger; *Vice-President*—Salvatore Sanfilippo; *Secretary*—Ronald R. Brown; and *Treasurer*—C. Louis Davis, of Coronado Paint Co.

Program Committee

Other members of the Program Committee were: Mr. Hendry, Mr. Link, Peter Caramello, of Davies Can Co.; Berger Justen, of Justen & Associates; Melvin L. Penn, of Kerr-McGee Chemical Co.; Thomas Holliger, of Union Carbide Corp.; Terry Walsh, of Kinsmen Corp.; Bernard T. Fisher, of SCM Pigments; Edward W. Siersma, of American Cyanamid Co.; James Wrasman, of Reichhold Chemicals, Inc.; Dan Dixon, of Freeport Kaolin Co.; and these spouses: Keen Hendry, Theresa Fisher, Denny Siersma, and Marilyn Wrasman.

Future Dates

The future annual meetings of the Southern Society will be: 1985–March 26–28, in Atlanta; 1986—March 25–27, in Savannah.

'Call for Papers' Announced for 1985 WCS Symposium

A call for papers has been issued for the Western Coatings Societies' 17th Biennial Symposium & Show to be held February 26–March 1, 1985 at the Disneyland Hotel & Convention Center.

The theme for the event, which will attract in excess of 2000 registrants, is "Tomorrow's Coatings—Today's Frontier." In keeping with this subject, the Symposium Technical Committee intends to present a varied program covering the current technology of coatings plus new processing and marketing concepts. Emphasis is expected on the changes in air quality regulations scheduled for implementation in 1985.

While papers should cover subjects of general interest to the Coatings Industry, they should detail fundamentals and the most recent technological advances. Papers will be divided into the following categories: Binders; Pigments and Extenders; Waterborne Coatings; High Solids Coatings; Low Energy Conversion Systems; Additives; Color; Manufacturing, Marketing and Management; Government Regulations; Computer Applications.

Original, not previously presented papers are required. Abstracts of 300–500 words in length should be submitted by June 1, 1984 to: Philip C. Bremenstuhl, Technical Committee Chairman, Fredericks Hansen Paint Company, P. O. Box 5638, San Bernardino, California 92412.

Complete information about the Symposium and Show can be obtained by contacting Richard C. Sutherland II, General Chairman, Symposium Headquarters, 11911 South Woodruff Avenue, Downey, California 90241.

CMU Presents "Colloids & Interfaces," May 21-25

"Colloids and Interfaces," a five-day seminar, sponsored for the ninth consecutive year, by Carnegie-Mellon University, Pittsburgh, PA, will be held May 21–25.

Designed specifically for anyone who works with adhesives, sealants, wetting agents, pigments, paints, printing inks, magnetic tapes, etc., this course will provide a foundation in the fundamentals as well as an introduction to the latest research techniques.

Tuition for the course is $825 which includes text, course notes, and laboratory fee. For more information contact Frank E. Nowak, Director of Post College Professional Education, 405 MMCH, Carnegie-Mellon University, Pittsburgh, PA 15213.

'Safety and Robotics' Is Topic of Golden Gate Mfg. Conference

The Golden Gate Society will present its Manufacturing Conference, "Safety and Robotics," June 18 at Sabella's Restaurant in San Francisco.

Presentations on safety will include topics on the handling and storage of materials and laws that affect these materials. In addition, the Stationary Source Div. of California will present an update of current projects and a perspective of California's air pollution control activities during this decade.

The program will also feature presentations on plant automation and the use of robots for painting.

Lectures include the following:

"Hazardous Waste Disposal, Local Ordinance"—Ken Slamon, Battalion Chief Fremont Fire Dept.

"Occupational Safety"—Nancy Finson, De Soto Chemical Co.

"Plant Safety"—Speaker to be announced. E.I. Du Pont de Nemours & Co.

"Hazardous Spills"—Robert Hirsch, Manager, Chemical Waste.

"Spray Painting Robot"—Michael Pascaru, Regional Sales Manager, Nordson Corp.

"Robotics in Finishing"—Norman Fender, Vice-President, Grayco Robotics

"Robotics and Electrostatic Spray"—William Teunzing, Technical Engineer, Binks Manufacturing Co.

"The Automated Plant"—Irv Wangness, Glidden Coatings & Resins.

"The Direction of California's Air Pollution Control Program"—Peter D. Venturini, Stationary Source Div., Calif. Air Resources Board.

Registration fee of $49 includes lunch and dinner.

For further information, or to register, please call E. "Bud" Harmon, Borden Chemical Corp., 41100 Boyce Rd., Fremont, CA 94538; (415) 657-4500.

Philadelphia Society To Hold Seminar On Anti-Corrosive Coatings

The annual seminar of the Philadelphia Society will feature as its topic, "Contributions of Components to Anti-Corrosive Coatings." The seminar will be held at the Airport Hilton Hotel in Philadelphia, May 14.

Presentations include the following:

"Considerations in the Formulation of Corrosion Inhibiting Paints on the Basis of Inorganic Barrier and Reactive Pigments"—Dr. Rolf H. Odenthal, Mobay Chemical Corp.

"A New Level of Performance in Acrylic Latex Based Corrosion Paints"—Dr. Robert N. Washburne, Rohm and Haas Co.

"The New Generation of Corrosion Resistant Zinc Phosphates"—Speaker from Heubach.

"Versatility of Epoxy Resins in Anti-Corrosive Coatings"—Harry Dickman, Consultant.

"New Lead and Chrome Free Anti-Corrosive Pigment"—Robert H. Dey, NL Industries/NL Chemicals.

"Chlorinated Vinyl Acrylic Latices for Steel Protection"—Marvin L. Caine, ICI Americas, Inc.

The seminar fee of $40 includes lunch.

For further information, please contact Barry Oppenheim, Seminar Chairman, at (215) 624-4400.

NEW YORK SOCIETY SCHOLARSHIP AWARDS

The New York Society for Coatings Technology offers several scholarships to college students of chemistry and chemical engineering, who are employed in the coatings and related industries, or who aspire to these industries, or who are children of people so employed.

Applicants must write to the Scholarship Committee, describing their current academic and extracurricular activities, the means of funding their education, and the reasons they should be considered to receive a Scholarship.

Responses should be sent by June 1984 to:

Marvin Wexler, Chairman
Scholarship Committee
c/o Troy Chemical Corp., Inc.
One Avenue L
Newark, N.J. 07105

People

Raymond Hurley has been named Product Manager for Thermoset Process Chemicals at Interstab Chemicals, Inc., New Brunswick, NJ. Mr. Hurley had been Laboratory Manager for Coatings Additives for the company. In his new role, he will be responsible for new product development, including production and commercial application. His function will also include market feasibility studies, pricing, inventory responsibility, as well as technical development of each new product. Mr. Hurley is a member of the New York Society.

Violet L. Stevens has been named a Research Associate in the Inorganic Chemicals Product Dept. of Dow Chemical Co., Midland, MI. She is a member of the Research and Development Group. Ms. Stevens is recognized for her development efforts in the application of chlorinated solvents to the industrial coatings market and for her role in launching market development efforts on the use of vinylidene chloride monomer for the production of coating resins.

Commercial Coatings Corp., Miami, FL, has announced the promotion of **Jack E. Benham** to Vice-President. Mr. Benham is a specialist in architectural coatings, caulkings, and waterproofing. He is a member of the Southern Society.

After 18 years of service, **Karl F. Giloth** has retired as President of Chemcentral Corp., Chicago, IL. He joined the company in 1966 as Vice-President and Director of Marketing.

The company also has announced the appointment of **Tom Shumate** to General Manager of Chemcentral/Louisville.

Dr. Ronald W. Kreis has been named Director of Research for Alcolac Inc., Baltimore, MD.

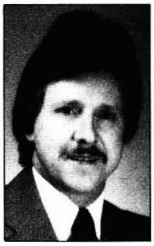
Several appointments have been announced by Dyco Chemicals and Coatings, Inc., Clearwater, FL: **Tom Brammer** to Executive Vice-President and Chief Operating Officer; **Robert M. Hourigan** to Vice-President of Technical Resources; and **Jerry Kimball** to Vice-President of High Performance Coatings.

Harshaw/Filtrol Partnership, Cleveland, OH has named **Dr. John B. Toogood** Vice-President of Sales, responsible for all Harshaw products.

Raymond Hurley

Violet L. Stevens

Thomas H. Cahir



Raymond Kinzig

Michael P. McCarthy has assumed the responsibilities of Regional Manager, Trade Sales, for the Midwestern region of The O'Brien Corp. He replaces **Douglas Miller**, who recently retired after 30 years of service.

In addition, **Thomas H. Cahir** has been named Vice-President, Operations, for the Midwestern region.

McWhorter, Inc., Carpentersville, IL, has announced the appointment of **Steven Lindberg** as Process/Project Engineer.

In addition, **Joseph McNiff** has been appointed Technical Sales Representative for the firm. A member of the Philadelphia Society, he will be responsible for the Mid-Atlantic states region.

Gale T. Collupy has joined Lukens Chemical Co., Inc., Westboro, MA, as Technical Sales Manager. He is a member of the New England Society.

Francine Shuster has joined the Midland Div. of The Dexter Corp., Waukegan, IL, as Senior Group Supervisor, General Industrial Laboratory. She will lead the group responsible for urethane and food release coatings development.

Central Can Co., Chicago, IL, has appointed **Daniel J. Gill** as General Manager—Sales, responsible for management of direct sales, representative sales, and marketing of the firm's container products. Mr. Gill joined Central Can in 1968 as a Sales Representative.

Gibson-Homans Co., Twinsburg, OH, has named **Edwin J. Hull, Jr.** Group Vice-President. Prior to his appointment, Mr. Hull served as Vice-President of Marketing. He will continue to be responsible for marketing and will also supervise all trade sales and national account sales for the firm.

Ferro Corp., Cleveland, OH, has named **Raymond Kinzig** Product Manager of Vedoc® powder coatings. Mr. Kinzig will be responsible for managing the quality control, customer service, and technical support for the Vedoc powder coatings operations.

Anthony L. Savedra has been appointed Los Angeles District Sales Manager for the Coatings Division of the firm.

Anthony W. Opipari was named Vice-President of Technology for the Automotive Finishes Group of United Technologies' Inmont Corp., Southfield, MI. Mr. Opipari is an active member of the Detroit Society.

Joseph A. Budash has joined Anvil Paints and Coatings Incorporated, Largo, FL, as Vice-President and General Manager. Mr. Budash formerly held the position of Vice-President of Research and Development for Scott Paper Corp. He is a member of the Southern Society.

American Hoechst Corp., Somerville, NJ, has announced the appointment of **Dr. Heinz K. Hofmeister** as Group Vice-President. He will be responsible for the Specialty Products group which produces industrial chemicals, colorants and auxiliaries, printing products, photoresists, and electronic printing systems.

In addition, **William E. Bartlett** was named District Manager of pigments for the company's Midwest territory.

Glidden Coatings and Resins Div. of SCM Corp., Cleveland, OH, has announced two new manufacturing heads. **J.C. Thomason** was named Vice-President of Manufacturing and Engineering, and **Phillip K. George** was promoted to Director of Manufacturing.

S. Leonard Davidson, Past-President of the Federation, has accepted the nomination of the Oil & Colour Chemists' Association to serve as Vice-President of the organization for 1984–1986 term of office.

The nomination by the Association is an honor bestowed on distinguished members who have also served as President of allied associations, such as the FSCT.

Mr. Davidson retired in 1983 from NL Industries, Inc., Hightstown, NJ, after a 40-year career in the coatings industry. He had served the company as Regulatory Affairs Specialist. In addition to being a Past-President of the Federation, Mr. Davidson has also served as Chairman of the Environmental Control Committee.

Union Carbide Corp. has announced the promotion of **Peter D'Amico** to the position of Manager Sales Services for the Specialty Chemicals Div. at their world headquarters in Danbury, CT.

Paul O. Kennedy, Vice-President of Trade Paint Sales for PPG Industries, Inc., Pittsburgh, PA, has retired after 41 years of service. Replacing Mr. Kennedy is **Robert F. Wilkinson,** former Vice-President of Manufacturing for the Coatings and Resins Group.

Also announced by PPG is the appointment of **William H. English** as General Manager of fluid printing inks for the Coatings and Resins Group.

Pratt & Lambert, Inc., Buffalo, NY, has elected **James R. Boldt, William F. Bensman,** and **Donald W. Smith** as Corporate Vice-Presidents of finance, materials management, and safety/environmental affairs, respectively.

John T. Yeager was promoted to Vice-President—Technical Director of Pratt & Lambert's Paint Division, Buffalo, NY. Mr. Yeager, formerly Technical Director of Sales, will be responsible for the Paint Division's laboratory operation, product development, and quality control programs. He is a member of the Western New York Society.

Bruce H. Todd was named Senior Market Manager for Industrial Coatings, Specialty Chemicals Group by Johnson Wax, Racine, WI.

Several appointments have been announced by Sun Chemical Corp., Pigments Div., Cincinnati, OH: **Peter Danco** to Vice-President—National Accounts; **Arthur Finn** to Vice-President—Sales; **Paul Klein** to Vice-President—Manufacturing; **Edward Wood** to Vice-President—Marketing and Sales; **John Ignatius** to Flush Research Manager; **Jeff Hamilton** to District Manager, West Coast; **Jeffrey Randolph** to Group Leader, Technical Services Dept.; **Robert Jancewicz** to Philadelphia Area Salesman; and **Tom Ashe** to New England Area Salesman.

Michael G. Bell has been appointed Executive Director of the Association for Finishing Processes of the Society of Manufacturing Engineers. Mr. Bell will devote specific attention to the activities of the active committees involved with radiation curing, powder coating, waterborne materials, high-solids coatings, and the other processes used in manufacturing and finishing.

Dennis L. Dalton has been appointed Manager of the Coatings and Plastics Chemicals Div. at Buckman Laboratories, Memphis, TN.

Wayne Chemical Corp., Milwaukee, WI, has appointed **W. Thomas Pettijohn** as Vice-President of the newly formed Wayne Pigment Corp. Mr. Pettijohn has been with Wayne Chemical for over three years, serving most recently as Sales Manager—Pigments. Prior to joining Wayne, he was associated with NL Industries, Inc. Mr. Pettijohn is a member of the Chicago Society.

Mozel Chemical Products Co., St. Louis, MO, has announced the promotion of **Richard N. Wagner** to District Manager. Mr. Wagner has been associated with Mozel for 19 years, most recently serving as Technical Sales Representative in the Memphis, TN area. He is a member of the Southern Society.

Also announced by Mozel were the appointments of **Joseph Melton** as Technical Representative and **Ruby Poole** as Inside Sales Coordinator.

Cook Paint and Varnish Co., Kansas City, MO, has announced the promotion of **Robert L. Pond** to the position of Product Manager, Automotive Coatings. Mr. Pond will direct the marketing activities related to the firm's specialized coatings for plastic and metal automotive parts and components.

James Steever has been named Vice-President of the Technical Group for Pigment Dispersions Inc., Edison, NJ. He was formerly associated with Norwood Industries as a Product Development Chemist.

Three top level officers at Finnaren & Haley, Inc., Philadelphia, PA, were recently appointed. **Daniel J. Haley**, most recently President, was selected Chairman of the Board; **Robert A. Haley**, Executive Vice-President, was appointed President; and **Bernard J. Burke**, Assistant General Manager in charge of plant operations and purchasing, moves up to the Executive Vice-President position. Mr. Burke is a member of the Philadelphia Society.

James R. Scott has been promoted to the position of Division Vice-President, Corporate Sales for Nalco Chemical Co., Oak Brook, IL. He will be responsible for the Process Industry Group of corporate sales.

Al McMichael has been appointed General Manager of Universal Color Dispersion. Prior to his appointment, Mr. McMichael was associated with Johnson Wax Co. as Director of the U.S. Specialty Chemicals Div.

The Spencer Kellogg Div. of Textron Inc., Buffalo, NY, has announced the following appointments: **George H. Wilhelm**—Vice-President of Marketing; **James Stanton**—Vice-President of Materials; and **James E. Tracewski**—Administrator of Health and Environmental Affairs.

Robert G. Jenkins has been appointed General Manager of Borden Chemical's Adhesives and Chemicals Div. He is based at division headquarters in Bellevue, WA.

Obituary

Walter F. Kuster, 1942-43 President of the Federation, died in Derry, NH, on February 9. He was 84.

After graduating from Bucknell University, Mr. Kuster began his career in the Fabrics and Finishes Div. of DuPont Co. as a Research and Development Chemist. He later joined Carpenter-Morton Paint Co., Everett, MA, as Technical Director, and retired from there in 1972.

In addition to serving as President of the Federation, Mr. Kuster also served as President of the New England Paint and Varnish Production Club (now the New England Society) in 1938 and chaired the Program Committee for the 1938 Annual Meeting.

Literature

Light Monitor For UV Sunlamps

A light monitor for an ultraviolet light exposure system is the subject of new literature. Discussed is a light monitor which offers monitoring capability for improved test-to-test correlation of results when analyzed on an ultraviolet exposure system. Contact Altas Electric Devices Co., 4114 N. Ravenswood Ave., Chicago, IL 60613, for bulletin #1340.

Acid and Blocked Catalysts

A new, four-page brochure is available to aid in the selection of catalysts for amino crosslinked coatings and inks. The properties of seven acid catalysts and six blocked acid catalysts are summarized. Recommended uses are discussed both by product and application. For a copy of the literature, contact King Industries, Science Rd., Norwalk, CT 06852.

Bead Mill

Literature is available on the history of the development and utilization of the small media continuous milling machines. "The Bead Mill" is available from Netzsch Inc., Dispersion Equipment Div., 119 Pickering Way, Exton, PA 19341.

Styrene-Acrylic Latex

A styrene-acrylic latex, primarily used for water-borne maintenance paints, is described in a 10-page booklet. Applications noted include light-to-medium duty water-borne maintenance paints that resist flash rusting over clean steel substrates. Formula suggestions are given for air-dry, water-borne maintenance paints based on this styrene-acrylic latex, including an alkyd-modified white coating suitable as a primer or topcoat, and a red iron oxide inhibitive primer for low-cost shop coat applications. General formulation techniques are discussed, and suppliers of applicable paint materials are noted. Properties of the latex and of typical formulations are illustrated in tables. Information is also provided on health effects and storage and handling of the latex. A copy of "UCAR Vehicle 422", designated F-48403, is available from Union Carbide Corp., UCAR Emulsion Systems, Dept. K3442, Danbury, CT 06817.

Cobalt Free Drier

Literature is available featuring a cobalt free drier, which achieves non-yellowing finishes and decreases coating embrittlement. Manufacturers of air drying and stoving systems could find the uses of the drier most beneficial. Contact Capricorn Chemicals Corp., Harmon Cove Towers, Secaucus, NJ 07094 for additional information.

Organic Specialty Chemicals

A new organic specialty chemical brochure is available which describes contract manufacturing services and chemical intermediates along with a list of chemical process capabilities. For further information, contact Art Katz, Morton Thiokol Inc./Morton Chemicals Div., 101 Carnegie Center, Princeton, NJ 08540.

Letters to the Editor

Reader Comments on Efficiency of Ball Mills

To the Editor:

On page 71 of the January 1984 issue [of the JCT] you state, "According to Mr. Cleaver, ceramic Ball Mills were early dispersion machines that gave way to the attrition mills. Attriter mills were ten times more efficient than ceramic Ball Mills."

In response to the question, "What is the normal output?," the reply on page 72 is, "A lot depends on the product, but we could say it is ten times faster than a conventional sandmill."

There is really no reason why he could not have said 20, 30, or even 100 times more efficient or faster; particularly when the definition of "efficient" is open to one's interpretation.

We would very much like to know on what basis such statements are made, since efficiency and speed are not interchangeable factors. To most manufacturers, efficiency means the costs to produce a given amount of product, and many of them find that Ball and Pebble Mills fit best into their production schedule.

For over 30 years, we have continually been told that Ball and Pebble Mills are things of the past, but, except during recessions, we have seen a constant increase in the number and size of such "obsolete" machines being used. Maybe it's because such mills will forgive operator mistakes, or just maybe they are more efficient than many people realize.

John M. Rahter
Sales Engineer
Paul O. Abbe, Inc.

Thank You

To the Editor:

Just a note of thanks for the "Comment" by Marco Wismer, "Coatings Technology—Pride and Accomplishment" (*see page 7 of February JCT*). Dr. Wismer is exactly on target when he refers to our industry as high tech. It gets boring at times when the general public and the media consistently consider only the computer and electronics industries as "high tech". A commitment to research in our industry is vital for the future and well-being of us all. Thanks again for one engaged in such a research commitment.

Richard M. Green
Director, R & D
EXPER-TEK Laboratories
Spokane, WA

Book Review

ORGANIC COATINGS: Science and Technology, Vol. 5

Edited by
G.D. Parfitt and A.V. Patsis

Published by
Marcel Dekker, Inc.
New York, NY
$75.00

Reviewed by
Dr. Thomas J. Miranda
Whirlpool Corp.
Benton Harbor, MI

This volume is the fifth in the series of collected papers presented annually at the Athens conference. Papers are from the Seventh International Conference in Organic Coatings Science and Technology. Included are results obtained from 21 invited papers and five short contributed papers.

Contained in this volume are the latest developments in organic coatings presented by leading experts in the field. Emphasis includes work on epoxy resins, powder, water-soluble coatings, and pigment technology.

This work, like its predecessors, provides the coatings technologist an excellent review of the current scientific and developmental advances being made in the field. This year the size has been reduced to 6×9 in an attractive binding. Unfortunately, the price will probably put it out of the reach of many who might profit from its contents.

CLASSIFIED ADVERTISING

COATING ENGINEER GROWTH OPPORTUNITY

Position involves R & D with advanced photosensitive materials, including coating, exposure, and processing of these materials for production of precision holographic optical elements. Candidate should have B.S. in engineering with 5 years experience in R & D and production/process procedures in polymeric coating technology. *Kaiser Optical Systems, Inc.* is a pioneer in the development of holographic optical elements. Excellent fringe benefits package and a fast growing, high technology environment. Send your resume and salary requirements to Kaiser Optical Systems, Inc., P.O. Box 983, Ann Arbor, MI 48106. Information will be held in complete confidence.

Coming Events

FEDERATION MEETINGS

(May 15-18)—Federation "Spring Week." Manufacturing Seminar on 15th and 16th; Society Officers on 17th; and Board of Directors on 18th. Galt House, Louisville, KY. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

(Oct. 24-26)—62nd Annual Meeting and 49th Paint Industries' Show. Conrad Hilton Hotel, Chicago, IL. (FSCT, 1315 Walnut St., Suite 832, Philadelphia, PA 19107).

1985

(May 14-17)—Federation "Spring Week." Seminar on 14th and 15th; Society Officers on 16th; and Board of Directors on 17th. Hilton Hotel, Baltimore, MD. (FSCT, 1315 Walnut St., Philadelphia, PA. 19107).

(Oct. 7-9)—63rd Annual Meeting and 50th Paint Industries' Show. Convention Center, St. Louis, MO. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

1986

(May 13-16)—Federation "Spring Week." Seminar on 13th and 14th; Society Officers on 15th; and Board of Directors on 16th. Sheraton Station Square, Pittsburgh, PA. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

(Nov. 5-7)—64th Annual Meeting and 51st Paint Industries' Show. World Congress Center, Atlanta, GA. (FSCT, 1315 Walnut St., Philadelphia, PA 19107).

SPECIAL SOCIETY MEETINGS

(May 14)—Philadelphia Society Seminar on "Contribution of Components to Anti-Corrosive Coatings." (Philadelphia) Airport Hilton Hotel. (Barry Oppenheim, McCloskey Varnish Co., 7600 State Rd., Philadelphia, PA 19136).

(May 15-16)—Cleveland Society for Coatings Technology 27th Annual Technical Conference, "Advances in Coatings Technology." (Richard Eley, Glidden Coatings & Resins Div. SCM Corp., 16651 Sprague Rd., Strongsville, OH 44136).

(May 16-17)—"Coatings Tech Expo '84." 3rd Biennial Convention & Exposition sponsored by New England Society for Coatings Technology. Sheraton Inn & Conference Center, Boxborough, MA. (Chairman Bruce Ocko, The Truesdale Co., Brighton, MA 02135).

(June 8-9)—Joint Meeting of St. Louis and Kansas City Societies for Coatings Technology. Kansas City, MO.

(June 18)—Golden Gate Society for Coatings Technology's Manufacturing Committee Symposium on "Safety and Robotics." Sabella's, San Francisco, CA. (Louie Sanguinetti, Jasco Chemical Co., P.O. Drawer J. Mountain View, CA 94042).

1985

(Feb. 26-Mar. 1)—Western Coatings Societies Symposium and Show. Disneyland Hotel, Anaheim, CA.

(Mar. 26-28)—Southern Society. Annual Meeting. Atlanta Hilton Hotel, Atlanta, GA. (Salvatore G. Sanfilippo, Reichhold Chemicals, Inc., P.O. Box 1610, Tuscaloosa, AL 35403).

(Apr. 25-27)—Pacific Northwest Society for Coatings Technology Symposium. Empress Hotel, Victoria, B.C. (Ottwin Schmidt, Helzer Canada Ltd., 8531 Cullen Crescent, Richmond, B.C., V6Y 2W9 Canada).

1986

(Mar. 25-27)—Southern Society. Annual Meeting. Hilton Hotel, Savannah, GA. (Ronald R. Brown, Union Chemicals Div., P.O. Box 26845, Charlotte, NC 28213).

OTHER ORGANIZATIONS

(May 13-18)—Robotics and Computer Controlled Automation. Owen Graduate School of Management, Vanderbilt University, Nashville, TN. (Ms. Mary Kelly, Program Director, Vanderbilt Univ., Nashville, TN 37203).

(May 14-18)—"Spray Finishing Technology Workshop" sponsored by Bowling Green State University and the DeVilbiss Co. (Judy Jennings, Bowling Green State University, Bowling Green, OH 43403).

(May 14-18)—"Basic Microcomputer Programming for Coatings" Short Course. University of Missouri-Rolla, Rolla, MO. (Cindy Sonewald, Dept. of Chemistry, UMR, Rolla, MO 65401).

(May 16-18)—"Appearance Science Workshop." HunterLab, Reston, VA. (Ms. V. Baca, HunterLab, 11495 Sunset Hills Rd., Reston, VA 22090).

(May 20-23)—ASTM Annual Meeting. Queen Elizabeth Hotel, Montreal, Que., Canada. (ASTM, 1916 Race St., Philadelphia, PA. 19103)

(May 20-23)—ASTM Committee D-1 on Paint and Related Coatings & Materials. Montreal, Que., Canada. (ASTM, 1916 Race St., Philadelphia, PA 19103).

(May 21-25)—Short Course on "Adhesion Principles and Practice for Coatings and Polymer Scientists." Kent State University, Kent, OH. (Dr. Carl J. Knauss, Chemistry Dept., Kent State Univ., Kent, OH 44242).

(May 21-25)—Short Course on "Corrosion and Its Control by Protective Coatings." Lehigh University, Bethlehem, PA. (Prof. Henry Leidheiser, Jr., Sinclair Laboratory #7, Lehigh University, Bethlehem, PA 18015).

(May 22-24)—Chemical Coaters Association. "Surface Coating '84." Bloomington, MN. (Matt Huertz, Chemical Coaters Assn., Box 241, Wheaton, IL 60187).

(May 23)—ASTM Symposium on "Review and Evaluation of Appearance: Methods and Techniques" sponsored by Committee E-12. Queen Elizabeth Hotel, Montreal, Canada. (Symposium Chairman, J.J. Rennilson, Retro-Tech, P.O. Box 3103, La Mesa, CA 92041).

(June 4-8)—Short Course on "Advances in Emulsion Polymerization and Latex Technology." Lehigh University, Bethlehem, PA. (Dr. M.S. El-Aasser, Dept. of Chemical Engineering, Sinclair Lab #7, Lehigh University, Bethlehem, PA 18015).

(June 4-8)—Short Course on "Thermal and Rheological Characterization of Coatings and Polymers." Kent State University, Kent, OH. (Dr. Carl J. Knauss, Chemistry Dept., Kent State Univ., Kent, OH 44242).

(June 4-15)—"Basic Course in Coatings." North Dakota State University, Fargo, ND. (Dr. Frank N. Jones, Polymers & Coatings Dept., NDSU, Fargo, ND 58105).

(June 6-7)—"Color Technology for Management" course. Rochester Institute of Technology, Rochester, NY. (Brenda Reimherr, T&E Center Seminar Coordinator, Rochester Institute of Technology, One Lomb Memorial Dr., P.O. Box 9887, Rochester, NY 14623).

(June 10-13)—"58th Colloid and Surface Science Symposium." Carnegie-Mellon University, Pittsburgh, PA. (G.D. Parfitt, Chemical Engineering Dept., Carnegie-Mellon University, Pittsburgh, PA 15213).

(June 11-15)—"Principles of Color Technology" course. Rochester Institute of Technology, Rochester, NY. (Brenda Reimherr, T&E Center Seminar Coordinator, Rochester Institute of Technology, One Lomb Memorial Dr., P.O. Box 9887, Rochester, NY 14623).

(June 11-15)—"Water-Borne Coatings" Short Course. North Dakota State University, Fargo, ND. (Dr. Frank N. Jones, Polymers & Coatings Dept., NDSU, Fargo, ND 58105).

(June 17-20)—Dry Color Manufacturers' Association's Annual Meeting. The Greenbrier, White Sulphur Springs, WV. (P.J. Lehr, DCMA, Suite 202, 206 N. Washington St., Alexandria, VA 22314).

(June 18-22)—"Principles of Color Technology" course. Rochester Institute of Technology, Rochester, NY. (Brenda Reimherr, T&E Center Seminar Coordinator, Rochester Institute of Technology, One Lomb Memorial Dr., P.O. Box 9887, Rochester, NY 14623).

(June 24-29)—"High Temperature and Coatings" Short Course. Stockholm, Sweden. (Continuing Education Institute—Europe, Rorstorpsvagen 5, S-612 00 Finspang, Sweden).

Advertisers Index

AMERICAN CYANAMID CO. . . . . Cover 3

COSAN CHEMICAL CORP. 32

DANIEL PRODUCTS CO. 2
DISTI, INC. 93

ECLIPSE SYSTEMS, INC. 102
ENGELHARD CORP., MINERAL & CHEMICALS DIV. 12
EXXON COMPANY, U.S.A. 15

GENSTAR STONE PRODUCTS CO. 100
GLEN MILLS INC. 102

MINOLTA CORP. 64

PFIZER, INC., MPM DIV. 20-21
POLYVINYL CHEMICAL INDUSTRIES, INC. 19

ROHM AND HAAS CO. 4-5, 16-17, 28-29

SCM PIGMENTS, SCM CORP. 80
SHAMROCK CHEMICALS CORP. . . . . Cover 4
SHERWIN-WILLIAMS CO. 99
SILBERLINE MANUFACTURING CO. 101
SOUTHERN CLAY PRODUCTS 88
SPARTAN COLOR CORP. 31

UNION CARBIDE CORP. . . . . Cover 2, 1, 10-11, 49
UNION CHEMICALS DIV. 7

Humbug from Hillman

Restaurant place mats seem to be the new source of southern American humor. Our latest was forwarded to us by Sal Sanfilippo, the transplanted Southern Society's Secretary. These definitions, for the benefit of unfortunate non-Southerners, were culled from the place mats of Rousso's in Mobile, Alabam, suh.

Dixie Dictionary

auto (should)—"I auto go to work, but Ahm tared."
ax (question)—"Ah ax you this."
abode (a piece of wood)—as "Han me a bode to hit this mule."
barn (hatched)—as "I was barn in Kentucky."
braid (lot braid)—what you eat when u'nins is out of bisquits
balks (a square thang)—like a "match balks"
cad (to tote)—as "I cad ma bride over the threshold."
cheer (whut you sit on)—"Pull up a cheer and set down."
did (not alive)—as "He's did."
fussed—what comes before second
far—a burnin' pile of sticks
gull—a young female human
heaven (having)—"A'm heaven some folks in foah dinnah."
ice cool—a school for younguns before college
lot (un-dark)—"Jeannie with the lot-brown hair"
pin (whut you keep hawgs in)—a hawg pin
rat cheer (not there) (here)—like "lay it rat cheer"
stow—a place that sells stuff
thud (whut comes after 2nd)—as "This only my thud mint julep."
tin-sin-stow (5&10)—"Les go in the tin-sin-stow."

• • •

Sal also notes that, to be a truly converted Southerner, you must have an important prerequisite, i.e.:

"You must have at least one colonel in your family history. I have looked up my roots and, lo and behold, I have found that my great granddaddies were colonels in the Sicilian army. As Sicily lies somewhere around 37 degrees latitude, it would put it well into the Southern category or someplace between Virginia and North Carolina border."

Sal's place mat reminded me that my files contained one sent in by Joe Boatwright from Aunt Maude, who hails from Myrtle Beach, S.C. It's especially appropriate in this election year.

Local Candidate for Sheriff Reports on Campaign

Below is a statement of expenses alleged to have been filed by a candidate for Sheriff in our county:

"Lost 134 hours of sleep, thinking about the election.

"Lost 2 front teeth and a lot of hair in personal encounter with an opponent.

"Donated 1 beef, 4 goats and 5 sheep to county barbecues.

"Gave away two pairs of suspenders, 4 calico dresses, $5.00 in cash and 15 baby-rattlers.

"Kissed 126 babies.

"Put up 4 stoves, kindled 4 fires and shook hands with 9,305 people.

"Walked 976 miles.

"Told 10,101 lies and talked enough to make in print 10 volumes.

"Attended 16 revivals and was baptized 4 times by immersion and twice by other ways.

"Contributed $50.00 to foreign missions.

"Courted 9 widows.

"Hugged 40 old-maids.

"Got bitten by dogs 9 times."

LOST THE ELECTION BY 2,648 VOTES.

• • •

Dave Platt, who is starting to read almost every day now, found the following in an unidentified magazine.

Compensation Dilemma

The following insurance reports were recently received by the Paint and Decorating Contractors Association of San Francisco:

"I was working on a ladder which had been against the back of a double trailer, and someone drove the rig away while I was on the ladder, causing me to fall to the ground."

"I was pouring paint out of a barrel. It was too heavy and my muscle busted and my entestings popped out in what they call a herneeia. It was in the lower part of my stomic."

"Was assisting in repair of 4" L.P. gas main—lit cigarette—boom—multiple burns all over body."

"Being careful of left ankle (that was sprained), stepped off porch and broke right ankle."

"I sprained my ankle the same way I sprained it before."

• • •

From the Ehrman Collection of phrases as found by Earl Hill in the *Rubber/Plastic News,* we have chosen a few of the choice ones—

"He works for the import-outport bank."

"He likes sitting there in his big executive snivel chair."

"Feasibility means you are able to fease."

"That needs some thinking about; let me go and regurgitate for a couple of hours."

"I wish someone would make a decision, I'm tired of hanging in libido."

—Herb Hillman